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16. ABSTRACT

Outdoor smog chamber experiments using automobile exhaust were performed in this study. The purpose of the study was to provide a data base that modelers could use to develop new, improved mechanisms for use in the Empirical Kinetics Modeling Approach (EKMA). Thirty-three dual smog chamber experiments were conducted. These included experiments (1) using exhaust from a 1979 Plymouth Volare or a 1972 Dodge Charger, (2) comparing exhaust from two cars using the same gasoline, (3) comparing synthetic auto exhaust with real auto exhaust, and (4) comparing auto exhaust from premium and regular gasoline. Mass spectrometry and high resolution gas chromatography were used to quantify the initial concentration of the auto exhaust organic species.

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Abstract

The purpose of this project was to provide a database that modelers could use to develop improved photochemical mechanisms for use in air quality models such as EKMA. Outdoor smog chamber experiments using automobile exhaust were performed in this study. The data have been processed, validated, and added to the existing data base for photochemical mechanism validation and testing.

Thirty-three dual smog chamber experiments were conducted in this project. These included:

- 13 experiments using exhaust from a 1979 Plymouth Volare;
- 24 experiments using a 1972 Dodge Charger;
- 8 experiments comparing exhaust from two cars using the same gasoline;
- 7 experiments comparing a whole-volume cryocondenser exhaust collection and transport system with exhaust from one of the automobiles above;
- 6 experiments comparing a synthetic exhaust mixture with exhaust from one of the automobiles above;
- 2 experiments to directly test an EKMA control strategy reduction;
- 2 experiments comparing exhaust from premium and regular gasoline for the same car at the same HC and NO_x concentrations;
- 2 experiments lasting 31 hours each.

In addition to the chamber tests, the cars were tested each year on the EPA dynamometers in the standard Federal Test Procedure (FTP), the New York City Cycle, and at high idle for emissions rate per mile and for emissions detail hydrocarbon composition and HC class fractions.

The detail HC compositions were subjected to extensive analysis. A double-focusing, magnetic sector mass spectrometer and capillary column gas chromatograph were used to analyze the exhaust. Mass spectra of approximately 90 peaks were used to identify the species in the exhaust. In the later chamber tests and experiments, a high resolution gas chromatograph was used to quantify the initial concentration of 102 species.

General findings were:

- direct injection of automobile exhaust from a vehicle operated in high idle, when split between the two chambers every one second, gave identical reactivity in the two chambers;
- direct injection of automobile exhaust in one chamber and cryogenically trapping the whole exhaust volume at the same time with subsequent evaporation of the trapped exhaust into the other chamber gave essentially identical results when the reactant masses were the same;
- direct injection of exhaust from one vehicle into one chamber and direct injection of exhaust from the other vehicle into the other chamber showed that, at the same HC and NO_x concentrations, the exhaust from the controlled vehicle was slightly more reactive;
- when the same vehicle was used to directly inject exhaust from premium gasoline into one chamber and exhaust from regular gasoline into the other chamber, the reactivities of the two sides were essentially the same;
- in two experiments using regular gasoline and different HC-to-NO_x ratios, a 60% reduction in the exhaust HC between the two chambers, at the same NO_x, resulted in a 30–35% reduction in peak ozone.

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1

Introduction

The Bureau of Mines (BOM) auto exhaust database has been used for more than 12 years to validate model predictions for ozone (O_3) as a function of oxides of nitrogen (NO_x) and hydrocarbons (HC). These data were generated by Basil Dimitriades during 1967–68 at the Bureau of Mines Research Center at Bartlesville, Oklahoma.[1,2]

The BOM database has been considered one of the best for understanding the relationship of O_3 to its precursors: it was reasonably complete, it was conducted at concentrations close to those in the atmosphere, and most importantly, it used real automobile exhaust.[3] The study used exhaust from a 1963 automobile equipped with a 183 in^3 engine operated in the 7-mode California cycle. Hydrocarbon concentrations ranged from 0.25 to 5.0 ppmC and NO_x concentrations ranged from 0.10 to 1.4 ppm. Thirty-one experiments were performed at nearly constant light intensity, temperature, and relative humidity. Each experiment lasted six hours.

In 1976, the BOM data were chosen as the basis for empirically adjusting the Dodge mechanism's propylene/n-butane fractions (the Dodge mechanism has no aromatics) to represent an appropriate HC reactivity.[4] That is, the fraction of propylene and n-butane were adjusted until the model predictions of O_3 agreed with the BOM chamber data. Demerjian, in a later study, also adjusted his mechanism's reactivity using the BOM data.[5]

Subsequently the Dodge mechanism and the assumptions of reactivity derived from the BOM data were incorporated into a computer program for producing O_3 isopleth diagrams (OZIPP).[6] These isopleth diagrams were, in turn, used in an EKMA procedure to estimate HC reduction requirements for urban areas. A major assumption in this entire process was that the urban atmosphere had the same O_3 formation potential as the BOM smog chamber with its automobile exhaust.

Need for New Data

Although it has been used, through OZIPP/EKMA, in the standard setting process, the BOM data base has four major problems:

- the experimental uncertainties of the data are large and do not provide a definitive test of mechanisms;[7]
- the analytical methods used in producing the data are unsatisfactory for today's modeling needs;
- the composition of today's automobile exhaust is different from that in the BOM study and some current mechanisms are extremely sensitive to compositional changes and;
- the contribution of automobile exhaust to the total urban mix reactivity is unknown; comparison with the reactivity of other synthetic urban mixes is necessary.

Significant knowledge about the photochemical process has been gained since the BOM experiments were performed. Kinetics mechanisms are the central components in today's understanding of these processes. The accuracy of the representation provided by the photochemical kinetics mechanism simulation has become the primary question. Only by comparison of model predictions with smog chamber data that was ***designed to test model accuracy*** can model validity questions be adequately addressed.[8,9]

Since the early 1970's EPA has sponsored a series of projects to develop suitable mechanisms and to produce experimental data to support and test these mechanisms.[10,11,12] These early chamber experiments were designed primarily to develop and test fundamental aspects of mechanism representation as opposed to simulating urban chemistry. For example, they focused on understanding formaldehyde chemistry, propylene chemistry, and on testing the correct representation of O_3 + olefin reaction products.[13] To expand the types of model developement issues that could be addressed with smog chamber data, we initiated another experimental program just before this exhaust project was started. The purpose of this "reactivity project" was to investigate model weaknesses in the representation of mixtures and to demonstrate how composition effected reactivity.[14] The reactivity study systematically produced smog chamber data using a series of mixtures covering the range from simple 3-component mixtures to complex 18-component mixtures. Also at the start of this exhaust project, yet another UNC project was producing smog chamber data under fully dynamic conditions (*i.e.* large dilution and continuous injection of reactants) to assure that model representation would work for typical atmospheric conditions as well as for the traditional static operating conditions of smog chambers.[15] Thus more than 300 experiments that addressed many fundamental mechanism development and testing issues would be available from the UNC outdoor smog chamber when this exhaust project was finished.

Until this project, however, no major smog chamber work utilizing automobile exhaust and designed to test model representation had been sponsored by EPA. The reasons that such chamber tests were needed are:

- automobile exhaust is extremely complex in its HC composition and all mechanisms for use in control predictions use a "compressed" or "lumped" representation of HCs; thus there was a need to produce chamber data that could be used by modelers to demonstrate that representations that worked for 5–15 species would also work for real (as opposed to synthetic) complex mixtures (with 150–200 species) such as those from automobile exhaust;
- on-road vehicles have a range of controls that affects the exhaust emissions composition and chemical models are expected to correctly respond to changes in emission composition as the controls are changed; thus there was a need to produce chamber data to demonstrate that model representations would work adequately for exhaust from both controlled and uncontrolled vechiles;
- on-road vehicles use different composition gasolines that affects the reactivity of the exhaust and chemical models are expected to correctly represent the effect of changing gasoline composition; thus there was a need to produce chamber data to demonstrate that model representations would work adequately for exhaust from vehicles using different types of gasolines such as regular and premium grades.

In the event of a model's failure to represent the exhaust chamber data correctly, the existing 300 experiments would be used to help "debug" the model. Thus there was no need to produce a completely independent set of exhaust/NO_x experiments, nor was it necessary to test all types of cars or all types of gasolines. The primary question was "Are the already developed HC representations in air quality models adequate to represent the range of variation likely to occur in urban simulations needed for control calculations?" Thus the complexity of the experimental design for this project was greatly reduced.

Purpose

The purpose of this research was to provide a database that modelers could use to develop, test, and improve mechanisms for use in control calculation methods such as EKMA. The operations for achieving this purpose were to:

- perform outdoor smog chamber experiments using automobile exhaust;
- process and validate the data, especially the exhaust composition data; and
- add the data to the existing database for testing photochemical mechanisms.

These new experiments used a controlled and an older, less-controlled automobile fueled with premium and regular gasolines and operated using standardized conditions. Improved characteristics of this exhaust database resulted from:

- the use of realistic physical conditions of sunlight, temperature, and humidity;
- the use of appropriate concentrations of precursors;
- testing of the cars on EPA dynamometers concurrent with a program to test a large fleet of 1975–82 in-use vehicles;
- improved methodology and analytical techniques.

Approach

The dual nature of the UNC outdoor smog chamber allows side-by-side experiments to be performed. When one factor is different between the two sides, for example the reactivity of a controlled versus an uncontrolled car's exhaust at the same total hydrocarbon and oxides of nitrogen concentration, the effect of the factor is immediately obvious.

While the side-by-side, dual experiments yield direct data about the reactivity effect of a particular factor, they present operational difficulties when using real automobile exhaust, *e.g.* obtaining matched initial conditions from two cars. A significant experimental effort went into determining how best to perform characterized auto-exhaust experiments in the dual outdoor chamber.

The automobiles used in this study were tested several times throughout the study on dynamometers at the Mobile Sources Emissions Research Branch (MSERB) at the Atmospheric Sciences Research Laboratories of EPA in Research Triangle Park, N.C. During the time of this work, MSERB was also testing a fleet of 46 in-use vehicles for volatile organic compound emissions (VOC Study).[16] Data from the Plymouth Volare used in this study were included in the VOC study database. More dynamometer data are included here, especially for the 1972 Dodge Charger. Not only were the standard emission measurements made during the tests of our cars, but also detailed analysis of the exhaust composition in several operating modes were determined. In some of these tests, gas chromatography/mass spectrometry was used to identify the individual HC species in the exhaust. These data, combined with the VOC study database, provide a means to estimate the general applicability of the chamber results to current fleets.

In the chamber tests, some exhaust hydrocarbon speciation, total NMHC, detailed aldehyde and oxygenates, CO, PAN, HNO_3, organic nitrates, NO_x, and O_3 data were obtained.

Data from the best model testing experiments reported here are available on a standard ANSI formatted magnetic tape, as are the other 300 experiments mentioned above. A description of the complete database, including the automobile exhaust experiments, is given in "Experiments to Test Photochemical Models: Phase II," an EPA report.[15] Information on availability of the data tape can be obtained by writing or telephoning:

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2

Background

Automobile Hydrocarbon Emissions

Emissions Standards

Table 1 gives the chronology of automobile hydrocarbon emission standards. This table also defines some terms and methods used in assessing compliance.

Effect of Controls on Emission Rates

The effect of the catalytic converter and other controls was illustrated in an EPA study of in-use vehicles.[17] The tailpipe emission rates for four vehicles with increasing degree of controls are given in Table 2 and are illustrated in Figure 1. These data show that there was nearly a factor of 10 reduction in tailpipe emissions across the four vehicles. Both regular and premium, summer and winter blended gasolines were used in the 1980 EPA study. The effects of these different gasolines on tailpipe emissions *rates* were very small (see Figure 1).

The EPA study also included the SHED evaporative emissions test and these results are included in Table 2 and in Figure 1. These data suggest that the tailpipe emissions only accounted for ≈40% of the total emissions of the 1963 car. Likewise, the tailpipe emissions accounted for ≈50% of the total in the 1977 car, for ≈60% of the total in the 1978 car, and for 20 to 60% of the total in the 1979 car. The evaporative emission rate was a function of the type of gasoline used, being larger for the higher vapor pressure, winter blended gasoline. This gasoline had a larger light paraffin content than the premium summer-blend gasoline.

Table 1. Automobile Hydrocarbon Standards

Year	Tail pipe[a] g/mi	Evaporative g/test[c]	Comments[b]
1972–74	3.4	2	carbon trap test
1975–77	1.5	2	carbon trap test
1978–79	1.5	6	SHED test
1980	0.41	6	SHED test
1981–83	0.41	2	SHED test

[a] Federal Test Procedure conducted on dynamometer: a constant volume sample is taken while the vehicle is cold started, driven on a 23 minute, 7.5 mile, non-repetitive, urban driving cycle, stopped for 10 mins. and hot started.

[b] The test method for evaporative emissions was changed from sampling around selected areas of the vehicle to the use of a Sealed Housing for Evaporative Determination. Two tests are conducted in SHED: Diurnal and Hot soak.

[c] A method for converting evaporative test results into an equivalent "g/mi" evaporative loss rate is:

$$\text{Evap (g/mi)} = \frac{\text{Di(g/day)} + 3.3 \text{ trips/day} \times \text{Hs(g/trip)}}{29.4 \text{ miles/day}}$$

where Di= diurnal evaporative emissions, and Hs= hot soak evaporative emissions. *N.B.* a 6 g/test result is equivalent to 0.44 g/mi.

It is evident from Figure 1 that both exhaust and evaporative emissions would be major factors in the reactivity contribution of automobiles in urban areas.

Effect of Controls on Emission Composition

The results of the 1980 EPA exhaust HC composition study are given in Table 3 and are also illustrated in Figure 2. According to the authors, the 1963 Chevrolet's composition was representative of the composition of nonconverter equipped cars. The 1977 Mustang's composition was similar to the that of 1975–77 converter equipped cars. The 1978 and 1979 cars had large decreases in olefin and aromatics and increases in paraffins compared to the older cars. These results, however, were only for the regular, winter-blended gasoline. It should be noted that the study was conducted in summer-like conditions even though a winter blend gasoline was used; the higher temperatures combined with the higher vapor pressure gasoline, may have distored the relative importance of evaporative and tailpipe emissions and compositions.

When premium gasoline was used in the same cars, the tailpipe composition was substantially different. The premium gasoline had 28% toluene and a total of 43% aromatics (Figure 2). This higher aromatic content in the fuel was reflected in the tailpipe composition which was 40% aromatic for the 1977 Mustang; the others were ≈30% aromatic (see Figure 2). Note that the reactivity of the premium gasoline exhaust, on an equal carbon basis, may well have been higher than regular gasoline exhaust reactivity because acetylene and some paraffins were replaced with more reactive aromatics.

The evaporative emission composition was also strongly dependent upon the gasoline composition and its vapor pressure (Table 3 and Figure 2). The vapor pressure (expressed as the Reid Vapor Pressure in $\mathrm{lb/in^2}$, *i.e.* the vapor pressure at 100°F) of gasoline is adjusted between winter and summer primarily by changing the amount of n-butane and n- and iso-pentane. Increasing the n-butane raises the vapor pressure. As illustrated in Figure 3, the trend has been to increase the vapor pressure. For cars with evaporative control systems, "break-through" of the charcoal canisters is an important factor in the composition of the evaporative emissions.

The composition of the regular, winter-blend evaporative emissions for all four cars in the 1980 EPA study was dominated by paraffins, primarily butane and pentanes (Figure 2, lower right). The fraction of aromatics emitted was quite small.

Table 2. Tail Pipe and Evaporative Emission Rates for In-Use Vehicles from 1980 EPA Study

Vehicle	Controls[a]	Fuel[b]	Tail pipe THC, g/mi	Evaporative THC, g/mi	Total THC, g/mi	%T/%E
1963 Chevrolet	PCV	RWL	4.03	5.57	9.60	42/58
1977 Mustang	EGR/CAT/PCV	PS	2.78	2.65	5.43	51/49
	FTC	RW	2.80	3.61	6.41	44/56
1978 Monarch	EGR/AIR/CAT	RS	1.03	0.20	1.23	84/16
	PCV/FTC&CC	PS	0.89	0.47	1.36	65/35
		RW	1.27	0.75	2.02	63/37
1979 LTD–II	EGR/AIR/CAT	PS	0.48	0.31	0.79	61/39
	PCV/FTC/CC	RW	0.51	2.39	2.90	18/82

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[a] PCV= Positive crankcase ventilation; EGR= exhaust gas recirculation; CAT= catalysis; FTC= fuel tank canister (charcoal adsorber); CC= carburetor canister (charcoal adsorber); FTC&CC= A single canister used for both fuel tank and carburetor.

[b] RWL= Regular winter leaded (69% paraffin, 5% olefin, 26% aromatic), 12.8 Reid vapor pressure; RW= Regular winter (67% paraffin, 7% olefin, 26% aromatic), 12.3 Reid vapor pressure; RS= Regular summer (65% paraffin, 7% olefin, 27% aromatic), 8.4 Reid vapor pressure; PS= Premium summer (49% paraffin, 8% olefin, 43% aromatic), 9.8 Reid vapor pressure.

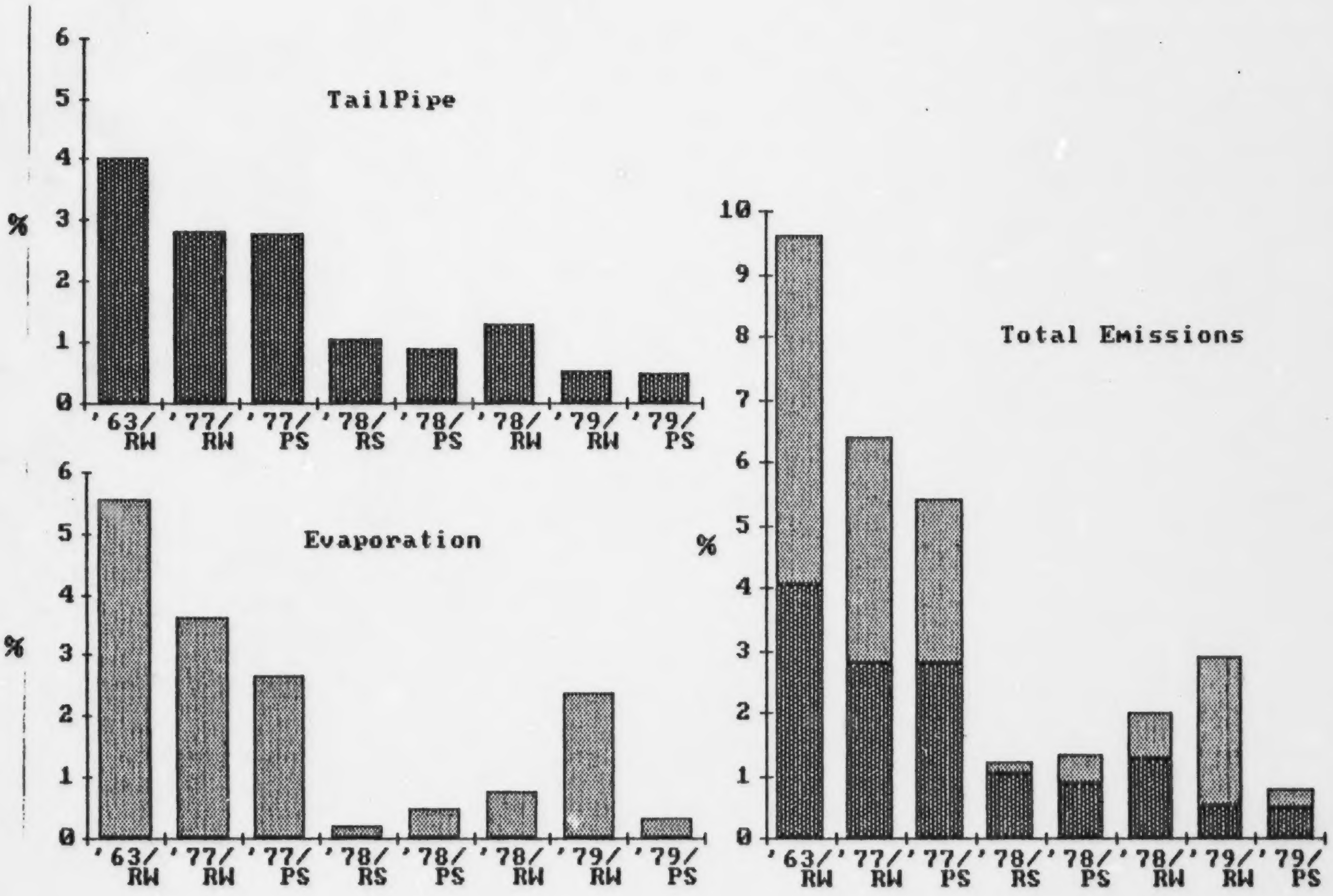


Figure 1. Tailpipe and evaporative emission rates for in-use vehicles in EPA study. See Table 2 for vehicle and fuel codes.

Table 3. Tail Pipe, Evaporative, and Aggregate Emission Composition for In-Use Vehicles from 1980 EPA Study, (wt%)

		Tail Pipe				Evaporative			Aggregate			
Vehicle[a]	Fuel[b]	P	O	A	Ac[c]	P	O	A	P	O	A	Ac
1963 Chevrolet	RWL	42.0	27.1	20.7	16.2	87.6	8.1	4.3	68.4	16.1	11.2	4.2
1977 Mustang	PS	43.2	16.0	40.7	0.2	75.1	11.5	13.4	58.8	13.8	27.3	0.1
	RW	54.7	21.6	23.4	0.3	82.4	11.4	6.1	70.2	15.9	13.7	0.1
1978 Monarch	RS	60.8	18.6	20.1	0.5	80.1	8.7	11.2	63.9	17.0	18.7	0.4
	PS	56.0	13.9	28.7	1.4	61.0	10.1	28.9	57.7	12.6	28.8	0.9
	RW	63.7	18.6	14.2	3.5	88.0	7.3	4.7	72.7	14.4	10.7	2.2
1979 LTD-II	PS	58.3	10.9	29.9	0.9	57.1	8.1	34.8	57.8	9.8	31.8	0.6
	RW	72.8	11.6	11.0	4.6	89.9	7.7	2.4	86.8	8.4	4.0	0.8

[a] See Table 2 for vehicle control systems.

[b] See Table 2 for codes.

[c] P=paraffins, O=olefins, A=aromatic, Ac= Acetylene.

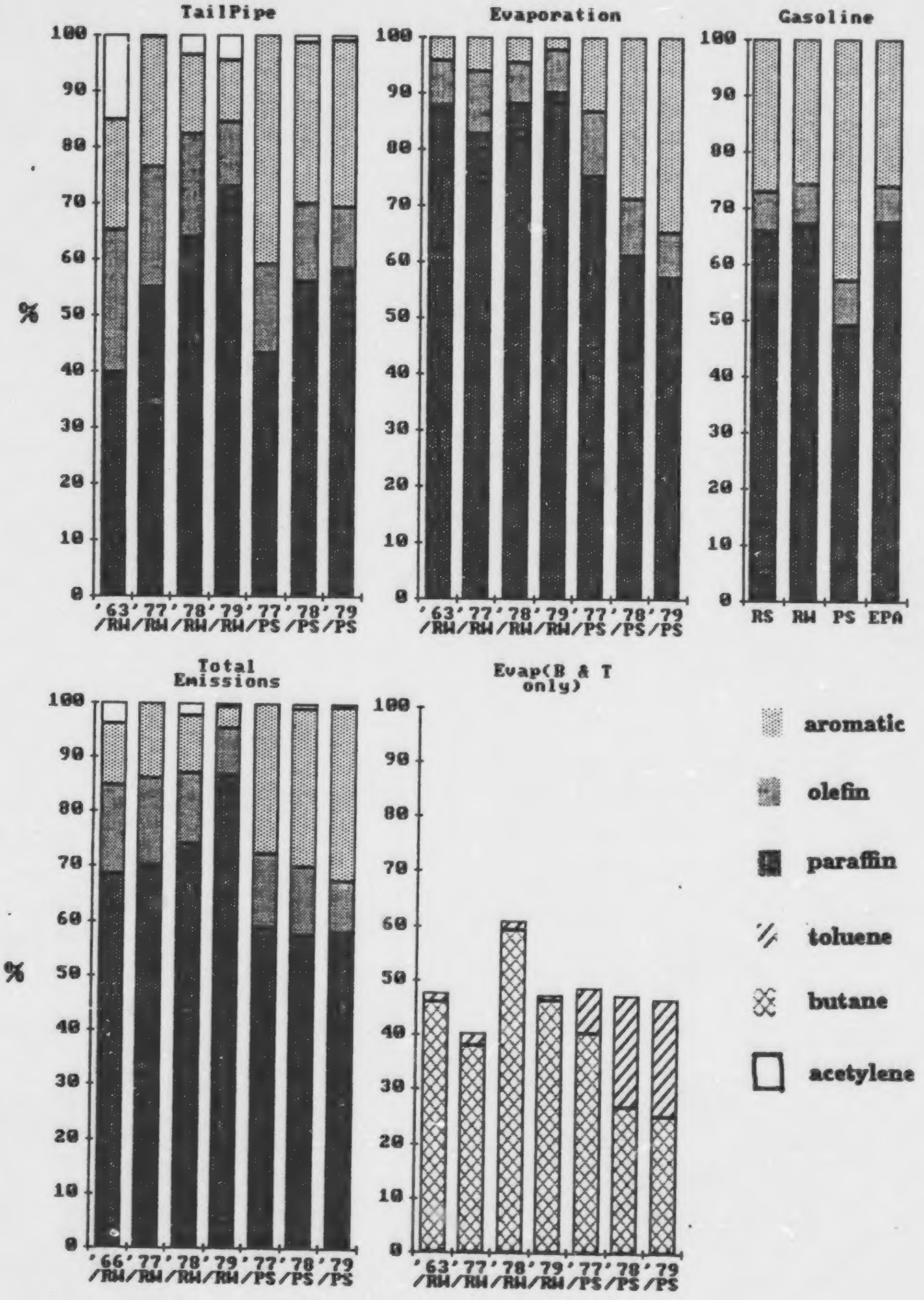


Figure 2. Tailpipe and evaporative emissions composition in 1980 EPA study. See Table 3 for vehicle and fuel codes.

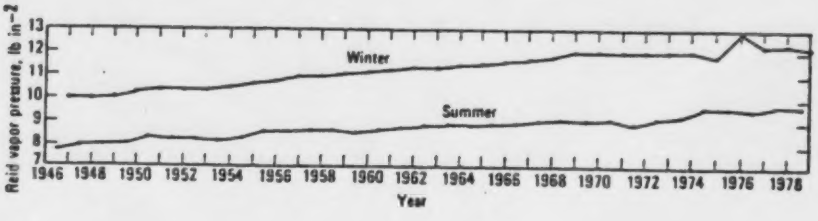


Figure 3. Gasoline Vapor Pressure Trends

This was in part due to the lower amount of aromatics in the regular blend and in part because, in this case, toluene was only a small fraction of the aromatics fraction.

The composition of the premium, summer-blended evaporative emissions, on the other hand, was relatively high in aromatics which was mostly toluene. This was, in part, a reflection of the fact that the gasoline had 26% toluene (Figure 2). Apparently the charcoal canisters were not very good at retaining toluene.

The aggregate emission composition data are an important part of the 1980 EPA emission study.

For the regular, winter-blend gasoline, the aggregate composition was nearly constant, except for the 1979 LTD (Figure 2). The LTD evaporative and tailpipe emissions were quite high in n-butane and pentanes.

For the premium, summer-blend gasoline, the aromatic fraction (and toluene) of the aggregate emissions increased with increasing controls and the paraffin fraction remained almost constant. Thus the mixture may have become more reactive over the last 5 years even though the mass emitted decreased substantially over the same period.

Clearly, the composition of the hydrocarbons emitted by the automobile are substantially influenced by the evaporative fraction and a smog chamber study should consider their effects.

Tailpipe Concentrations of Hydrocarbon

In another study of in-use vehicles, MSERB/EPA[18] tested a range of 1970 to 1981 cars on the dynamometer. Table 4 identifies the make and year of several of these vehicles and gives the THC and NO_x emissions rate from the entire FTP test, *i.e.* for the cold start, transient portion (first 8.4 minutes), for the warmed-up, stabilized portion (the next 14.6 minutes), and for the hot start, transient portion (another 8.4 minutes after a 10-minute engine-off period). Table 4 also reports the average tailpipe concentration of HC and NO_x from just the first 8.4 minutes cold start portion. For the newest catalytic cars (such as the Electra or Omega in Table 4), the tailpipe HC concentrations are usually much lower in the stabilized and hot start portion of the FTP test because, after the first 8 minute period, the catalyst is usually hot and working.

If it is assumed that we sample directly from the tailpipe, Table 4 gives the liters of exhaust that would be needed to produce 1.0 ppmC of HC in each side of the UNC chamber (chamber volumn is 150,000 liters each side). Also included are the NO_x concentrations and HC-to-NO_x ratios that would result from the injection of this exhaust. Except for the noncatalytic Impala and the incorrectly fueled Mustang, the HC-to-NO_x ratios resulting from exhaust of these cars are quite low.

Figure 4 shows the approximate location of these initial conditions on a standard Dodge isopleth diagram. Three of the points could not be plotted because of the high NO_x; the HC-to-NO_x ratio lines for these were plotted however. This plot allows an estimate of how much O_3 might be formed in the chamber. It suggests that the ozone formation might be quite low in those from new cars such as the Electra and the Omega. Thus, the newest vehicles, with the most efficient converter systems, most likely would not produce enough HC to test models adequately.

Table 4. Tail Pipe Emission Rates and HC, NO_x Concentrations

Vehicle, year	Whole FTP (23 mins) Emissions, g/mi		Average for 505 sec after Cold Start, FTP Tail Pipe, ppm(C)		Volume Exhaust for 1.0 ppmC	Resulting Chamber NO_x, ppm	Chamber HC/NO_x ppmC/ppm	. HC/NO_x in Chamber for 60L exhaust Sample
	HC	NO_x	HC	NO_x				
Econoline 1970	3.14	5.15	2962	1298	51.6	0.44	2.3	1.16/0.51
Impala 1973	3.48	2.54	3636	466	42.1	0.13	7.8	1.93/0.18
Mustang 1977[a]	2.94	1.60	3598	590	42.6	0.16	6.1	1.41/0.23
Aspen 1977	2.30	6.09	4108	1255	37.2	0.31	3.3	1.61/0.49
Honda 1979	2.67	2.77	5050	1049	30.3	0.21	4.8	1.98/0.41
Electra 1981	0.72	0.71	1383	260	110.6	0.19	5.3	0.54/0.10
Omega 1981	0.22	0.81	469	328	326.2	0.70	1.4	0.18/0.13

[a] This Mustang had been misfueled with leaded gasoline which deactivated the catalytic control system.

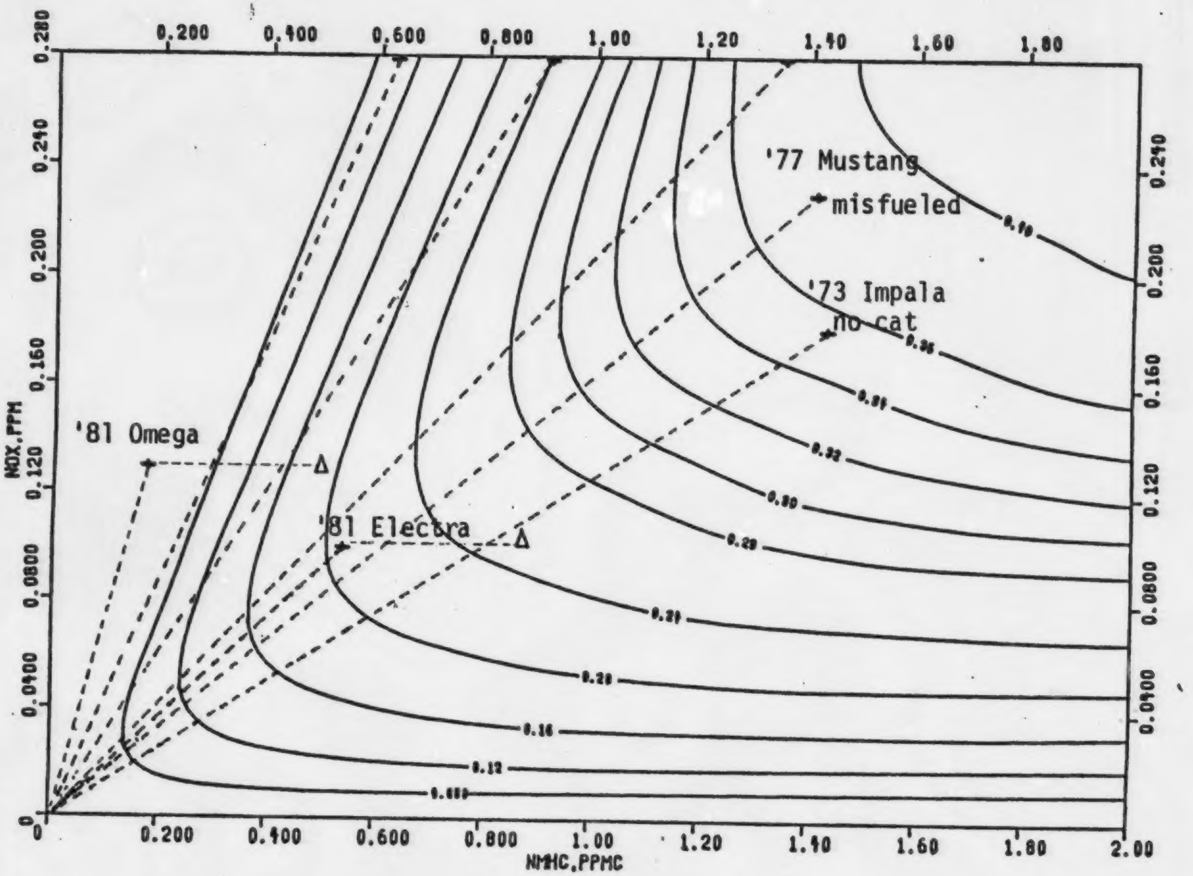


Figure 4 . Dodge Isopleth with Test Points using 60 1 exhaust sample (+), and using exhaust plus evaporative (**Δ**).

Automobile Exhaust Detailed Hydrocarbon Analysis

Complexity Issue

A major problem with analyzing automobile exhaust is that, although more than 200 hydrocarbons can be separated readily by gas chromatographic procedures, less than 20 compounds can represent nearly 75% of the mass. This means that there are nearly 180 compounds which are present at between 1.0% and 0.01% of the NMHC. Compounds, which individually may only represent ca. 1.0% of the NMHC, may, when summed together, be very important in affecting the total mixture reactivity (*e.g.* butenes).

Graphic illustration of this complexity is given in Figure 5. Three "linechromatograms," in which the percent of total NMHC of each compound is plotted as a function of the compound's retention time for a UNC exhaust sample are shown. All three chromatograms are for the same analysis, only the scales have been changed. In the Top Left plot, the total mixture is shown on a 10% carbon full scale plot; in the Top Right plot the total mixture is shown on on a 1% carbon full scale plot; and on the Bottom Left plot only the compounds present *at more than* 1% of the carbon are ploted (only 22 compounds). Another way of illustrating this complexity is in Figure 6 which shows the number of compounds that account for a given fraction of the mixture.

The complexity factor also impacts the number of analyses that can be conducted in a chamber or dynamometer run. An analysis capable of resolving more than 200 HCs requires sub-ambient temperature programming of a capillary gas chromatographic column and requires up to one-half a day to do correctly. This is followed by significant data processing to identify and quantify the important compounds. Furthermore, the daily analyses must be supported by many days of calibration and identification of species, generally by use of a gas chromatographic/mass spectrometer at a cost of about $1000 per day. This work should be done with the same column used in the daily analysis, making the analytical system less available for production work.

Instruments that attempt to bypass the separation of the compounds and analyze the "whole sample," such as total hydrocarbon or NMHC analyzers, in general, have been unsuccessful. On these instruments, individual compounds and even compound classes such as aromatics, aldehydes, and methane may exhibit

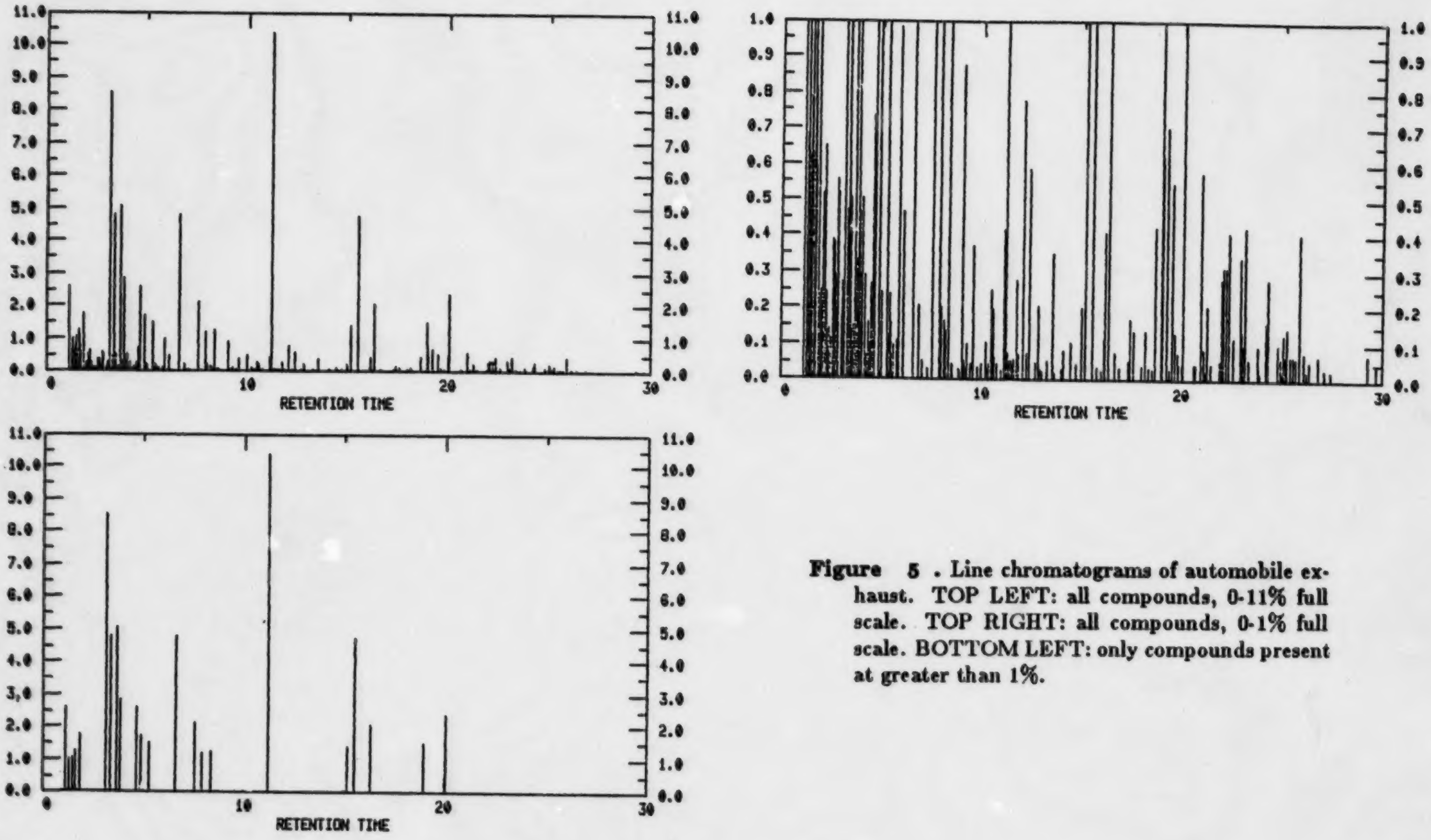
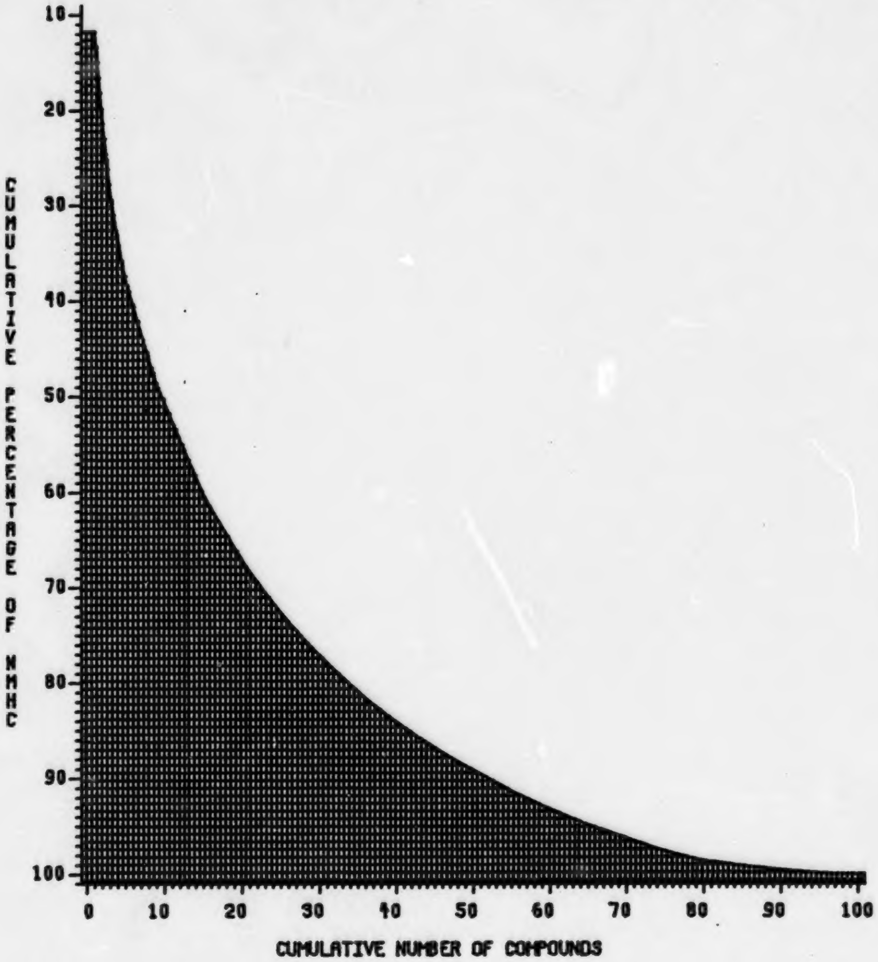


Figure 5 . Line chromatograms of automobile exhaust. TOP LEFT: all compounds, 0-11% full scale. TOP RIGHT: all compounds, 0-1% full scale. BOTTOM LEFT: only compounds present at greater than 1%.



CUMULATIVE % NMHC VS.
CUMULATIVE # OF COMPOUNDS

Figure 6. Fraction of NMHC represented by a given number of compounds in descending order for the MSB 1982 tests of the Dodge Charger, NYCC.

different responses making it difficult to apply calibration factors to the instrument responses without prior knowledge of the sample composition. Further, these instruments depend upon a small difference in two relatively large numbers (*e.g.* NMHC = THC $-CH_4$), a noise- and error-prone process, which contributes uncertainty to the HC concentrations.

Modeler's Needs

Models to be tested with the data generated in this project use some form of "lumped" or "surrogate-species" to represent the HC. These models require that the HC species present in the complex exhaust be classified into the various input forms used by the models.

All current models represent, *at a minimum,* the HC classes of paraffin, olefin, aromatic, and carbonyl or aldehyde; the two most likely-to-be-used models, the Carbon Bond series and the Atkinson-type models, have at least two species, one of low reactivity and one of high reactivity, in each of the HC classes or have explicit representation of the most common species. These models can use specific information on n-butane and iso-pentane, ethylene, propylene, toluene, and formaldehyde.

In addition, modelers need to know how to classify the remaining sample carbon after the above species have been taken into account. Thus, this project needed to supply modelers with a good estimate of the total non-methane hydrocarbon in the experiment, with the concentrations of the primary or major reactive species, and with sufficient information to divide the remaining un-speciated carbon into the various HC classes used in the models. The last need suggests that the composition of the exhaust must be studied in detail. Realistic chamber conditions, however, generally preclude this type of analysis for the actual run conditions unless very special analysis techniques are used. Detailed speciation for run injections was only performed for a few experiments; detailed speciation of exhaust samples was performed during dynamometer tests.

3

Program Design

Choice of Experimental Conditions

Factors Considered in Experimental Design

There were a wide range of experiments that could have been selected for this project. Resources and time limited the choices. The factors which were considered in the experimental design and selection were:

- the need to have both controlled and uncontrolled vehicles;
- the need to use both regular and premium gasolines;
- standard automobile operating conditions, sample generation and collection
- range of conditions necessary for mechanism testing
- characteristics of outdoor smog chamber and scheduling.

Goals

The first goal was to demonstrate that automobile exhaust runs could be satisfactorily performed in the dual outdoor chamber. That is, it was important to show that exhaust could be equally or uniformly injected into the chambers, and that the resulting mixtures in the two chamber halves would have equal photochemical reactivity.

The second goal was to develop a system that would allow us to take advantage of the MSERB/EPA dynamometer facility, both as a resource to characterize the automobiles used and as a potential source of controlled reactant mixtures. If we could use the already existing, complex gas chromatographic, exhaust analysis system at MSERB, this project would not have to develop extensive gas chromatographic systems at the research site. This meant, however, that we had to develop a method to sample and transport large quantities (> 60 liters) of raw exhaust without affecting the reactivity or composition of the exhaust. A cryogenic sampling system (called a cryocondenser) was developed to satisfy the latter need. It, in turn, had to be tested using the chamber.

The third goal was to explore the range of conditions likely to change the reactivity of automobile exhaust.

Run Strategy

The general strategy used to plan outdoor experiments was to arrange the proposed experimental runs in a priority order and to perform the highest priority experiment until a satisfactory combination of weather, instrument status, and initial conditions had been achieved. Prior experience demonstrated that it was not possible to forecast the type of weather needed for a good model testing run with better than a 50% chance of being correct. A second limitation was the difficulty of balancing the initial conditions, given complex sources like automobiles. A third factor, likelihood that all the instruments needed to quantify the HC mixture work satisfactorily, when combined with the other limitations, resulted in a yield of satisfactory runs of about one run for four attempts.

In listing the runs, the simplest type run that provided useful information was usually given a high priority. If the run proved simple to perform, then more complex runs were moved up in priority. In this manner, the priority of plan runs was based upon the outcome of previous runs. If the simpler runs resulted in a un-expected outcome, then they were usually repeated to verify the results before proceeding to more complex runs.

This strategy sometimes results in the more complex runs having their priorities lowered to the point that the project runs out of good weather or time before they are ever performed. On the other hand, the more fundamental questions are usually answered satisfactorily.

The general priority list of runs selected was:

- test chamber side-to-side performance with automobile exhaust injected directly from the tailpipe of the vehicles;
- test the cryocondenser sampling performance and its effect on the exhaust reactivity;
- test exhaust reactivity from controlled vs. uncontrolled cars;
- test exhaust reactivity from different gasolines in the same car and in different cars;
- test the effect of different operation modes on exhaust reactivity;
- test synthetic vs. real exhaust reactivity;
- test the effect of EKMA-style controls, *e.g.* same NO_x, different HC from the same car;
- test the effects of specific compositional changes in exhaust.

Some Design Problems

There were several factors that complicated and modified the design:

- the MSERB dynamometers and fuel source were located 40 miles from the UNC chamber; this meant that
  - transport of sample was necessary;
  - there were communication and scheduling problems;
- MSERB/EPA did not have a fixed "test" fleet; this meant that
  - we had to find and maintain our own cars;
  - MSERB had to characterize the cars and later in the program they were frequently busy with their own projects;
- exhaust composition work was more complex and effort consuming than original thought; this meant that
  - there were problems that were caused by having different instruments in different locations with different techniques and standards;
  - significant analytical development effort was eventually necessary at the end of the project;
- finally, the funding cycle was out of step with the run season; good run weather for outdoor experiments is between mid-May and late-October; the project was

initially funded in mid-summer.

These factors modified the choice of experiments, sometimes resulted in delays, and prevented the program as planned from being completed.

Planned Experimental Conditions

Table 5 presents the planned experimental conditions and the purpose of the experiment. This was an ambitious program; we did not expect to complete the entire program in the two summers available. Despite this many of the highest priority goals were achieved.

Table 5. Planned Automobile Exhaust Experimental Conditions

Operating Conditions Tests:

Run	Injection Source	Type	Comments	Purpose and Expected Outcome
1R	'72 Dodge -NL Regular -direct injection	Matched NMHC		How important is the car type (controlled, uncontrolled) when the gasoline and the total NMHC and NO_x are the same?
1B	'79 Plymouth -NL Regular -direct injection	Matched NO_x		Gasoline and matched concentrations will dominate car type (*i.e.* little difference).
2R	'72 Dodge -NL Regular -direct injection	Matched NMHC		How important is the gasoline composition when everything else is the same (for uncontrolled car)?
2B	'72 Dodge -NL Premium -direct injection	Matched NO_x		Gasoline type will dominate (*i.e.* large difference).
3R	'79 Plymouth -NL Regular -direct injection	Matched NMHC		How important is the gasoline composition when everything else is the same (for controlled car)?
3B	'79 Plymouth -NL Premium -direct injection	Matched NO_x		Gasoline type will dominate (*i.e.* large difference).
4R	'72 Dodge -NL Regular -direct injection	Matched NMHC	Hi-idle injection	How important is the operating mode when everything else is the same (for uncontrolled car)?
4B	'72 Dodge -NL Regular -cryocondenser	Matched NO_x	FTP dynamometer sample	Small difference with Hi-idle lower in reactivity.
5R	'79 Plymouth -NL Regular -direct injection	Matched NMHC	Hi-idle injection	How important is the operating mode when everything else is the same (for controlled car)?
5B	'79 Plymouth -NL Regular -cryocondenser	Matched NO_x	NYCC dynamometer sample	Small difference with Hi-idle lower in reactivity.

HC-reduction Tests:

Run	Injection Source	Type	Comments	Purpose and Expected Outcome
6R	'72 Dodge -NL Regular -direct injection	Different NMHC	Three-to-one ratio NMHC	Demonstrate direct effect of HC reduction (uncontrolled car).
6B	'72 Dodge -NL Regular -direct injection	Matched NO_x	NO_x balanced by tank injection	Many SIP's estimate a 60% reduction. Big difference expected.
7R	'79 Plymouth -NL Regular -direct injection	Different NMHC	Three-to-one ratio NMHC	Demonstrate direct effect of HC reduction (controlled car).
7B	'79 Plymouth -NL Regular -direct injection	Matched NO_x	NO_x balanced by tank injection	Big difference expected.

Synthetic Exhaust Tests:

Run	Injection Source	Type	Comments	Purpose and Expected Outcome
8R	'72 Dodge -NL Regular -direct injection	Matched NMHC		Compare direct autoexhaust with synthetic autoexhaust (uncontrolled car).
8B	Synthetic Autoexhaust	Matched NO_x	6 HC-compound mixture & ald.	Expect some difference with only two compounds per class.
9R	'72 Dodge -NL Regular -direct injection	Matched NMHC		Compare direct autoexhaust with synthetic autoexhaust (uncontrolled car).
9B	Synthetic Autoexhaust	Matched NO_x	12 HC-compound mixture & ald.	Expect very small difference with four compounds per class.

Reactivity Modification Tests:

Run	Injection Source	Type	Comments	Purpose and Expected Outcome
10R	'79 Plymouth -NL Regular -direct injection	Matched NMHC		Determine reactivity contribution of additional formaldehyde (controlled car).
10B	'79 Plymouth -NL Regular -direct injection	Matched NO_x	10 % additional formaldehyde	Expect some increase in reactivity compared to reference run (Run 13).
11R	'72 Dodge -NL Regular -direct injection	Different NMHC		Determine reactivity contribution of additional exhaust olefins (uncontrolled car).
11B	'72 Dodge -NL Regular -direct injection	Matched NO_x	20 % additional propylene	Expect larger difference than in reference run (Run 13).
12R	'72 Dodge -NL Regular -direct injection	Different NMHC		Determine reactivity contribution of important exhaust aromatics (uncontrolled car).
12B	'72 Dodge -NL Regular -direct injection	Matched NO_x	20 % additional 1,2,4-tri-methyl-benzene	Expect large difference when compared to the reference run (Run 13).
13R	'72 Dodge -NL Regular -direct injection	Different NMHC		Determine incremental reactivity of exhaust for reference in the above runs.
13B	'72 Dodge -NL Regular -direct injection	Matched NO_x	20 % additional exhaust	Expect less than 20 % increase in ozone.

4

Methods

Facilities and Vehicles

Outdoor Chamber

The UNC Outdoor Smog Chamber is located in a rural area away from major pollution sources.[19] The chamber is a 300,000-liter, rigid external A-frame, Teflon film chamber divided into two equal halves by a Teflon wall. The dual chamber design is used to perform side-by-side comparison experiments. It uses natural sunlight and ambient temperatures and humidity. It is purged overnight with rural ambient air. Instruments are timeshared on the two sides. The chamber and instrument operation and the data acquisition are controlled by a PDP-11 computer. A full facilities description is given in Appendix A. A complete analytical system description, including the mass spectrometry facility, is given in Appendix B.

Dynamometer Facility

The EPA dynamometer facility is located ca. 40 km from the chamber at the Mobile Sources Emission Research Branch (MSERB/EPA) in the Research Triangle Park. Like the outdoor chamber, these dynamometers are complex devices requiring sophisticated analytical gear and significant technical support to operate.

We were fortunate to have the support of Dr. Ron Bradow and Mr. John Sigsby of EPA, and John Lang of Northrop Services, Inc. This group not only performed the dynamometer tests on the UNC vehicles, they also performed HC species analysis for exhaust samples collected during the dynamometer tests.

Automobiles Used In Project

An ideal situation for this project would have been to use automobiles that had a long history of dynamometer performance measurements and a uniform and regular maintenance program. Unfortunately, no vehicles that met these criteria were available for the two year period of this project.

Instead two cars that were available full time to the project were used. One was a State of North Carolina Motor Pool vehicle that was "rented" for the duration of the study. The other vehicle was a private, second-car of one of the project staff. More complete descriptions of these vehicles are:

- **1979 Plymouth Volare**—This car was a 225 cubic inch, 6–cylinder, 2–barrel unstaged, catalyst-equipped vehicle with 37,262 miles at the start of the project (March 1982) and 53,946 miles at the end of the project (March 1984). It was owned by the State of North Carolina (s/n 4104595), and for the most part, received only standard motor pool service by the University. During the October 1983 dynamometer tests, however, MSERB/EPA did replace the carburetor with a new factory carburetor. The late October and November 1983 chamber tests, and the March 1984 dynamometer tests and hydrocarbon analysis were performed with the new carburetor. This vehicle was one of the five 1979 cars included in the MSERB/EPA VOC study.[VOC]
- **1972 Dodge Charger**—This car was a 318 cubic inch, V–8, 2–barrel unstaged vehicle with PVC pollution control and a carbon canister. It had 116,000 miles when the experiments were run. Except to drive to EPA for the dynamometer tests and for re-fueling at EPA, the car was not driven during the entire study period. This car was owned by an employee of the project and had received no special service.

Dynamometer Methods

The vehicle test procedures used by MSERB/EPA in this work were, for the most part, those described in the Code of Federal Regulations for emissions certification.[20] In the Federal Test Procedure (FTP) (Figure 7), the dynamometer test consists of two runs: the first, a "cold" start test, after at least a 12-hour park, and the second, a "hot" start test, following the first test by a 10 minute engine-off wait.

On the dynamometer, the car is driven on an Urban Dynamometer Driving Schedule (UDDS) which specifies, second by second, the vehicle speed. The "trip" is a 23-minute, 7.5-mile, non-repetitive cycle with 16 stops. During the dynamometer tests, a constant volume sample is taken. Three different bags of emissions are collected: the first is collected during the "cold" start transient portion which lasts for 505 seconds (8.4 min.) and has an average speed of 25 mph; the second bag is filled for the remainder of the first test in the stabilized portion of the cycle at an average speed of 16 mph; the third bag is collected from the "hot" start repeat of the first 505 seconds of the UDDS, again at an average speed of 25 mph. The results of each bag are weighted 0.43, 1.0, and 0.57 to produce the total test emissions; the stabilized portion of the "cold" start run is assumed to be the same as the stabilized portion of the "hot" start run, and the latter is omitted.

To the FTP were added several other driving schedules: the New York City Cycle (NYCC); the Crowed Urban Expressway cycle (CUE); steady state cruising at constant speeds (SS–30, SS–50); and high and low speed idles. The average speed in the FTP is about 19.5 mph; in the NYCC the average speed is 7 mph; and in the CUE it is 35 mph.

Example of Dynamometer Test Series

To illustrate the methods, the results of the first series of dynamometer tests for the Volare are given in Table 6. Because the exhaust was to be used as a chamber injection source, the actual tailpipe concentrations in ppm are listed in Table 6, as well as the standard emissions rates of g/mi.

The Volare was put through the standard sequence used to test compliance with EPA emission standards (Figure 7). The gas tank was pumped out and MSERB-stocked Amoco Premium gasoline was used to half-fill the tank. The car stood overnight in the test facility and was driven on the dynamometer the next day.

The Federal Test Procedure, evaporative shed test, the New York City Cycle, the CUE cycle, steady-state cruising at constant speed (SS– 30 and SS–50), and two idle speed tests were performed. The FTP and NYCC tests were repeated on the next day.

The first 505 seconds of the FTP includes a cold start and warm-up of the catalyst system and should give a high tailpipe HC concentration. Indeed this was

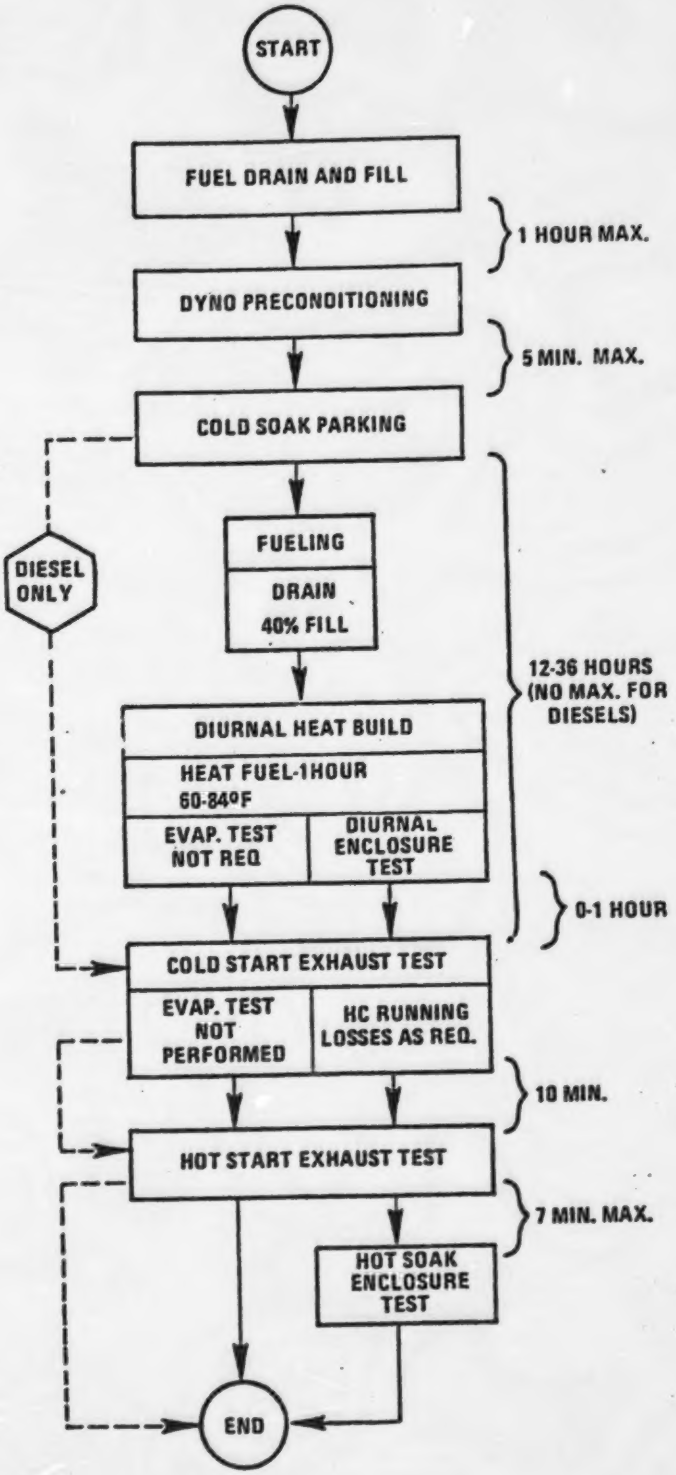

START
FUEL DRAIN AND FILL
1 HOUR MAX.
DYNO PRECONDITIONING
5 MIN. MAX.
COLD SOAK PARKING
DIESEL ONLY
FUELING
DRAIN
40% FILL
12-36 HOURS (NO MAX. FOR DIESELS)
DIURNAL HEAT BUILD
HEAT FUEL-1HOUR
60-84°F
EVAP. TEST NOT REQ
DIURNAL ENCLOSURE TEST
0-1 HOUR
COLD START EXHAUST TEST
EVAP. TEST NOT PERFORMED
HC RUNNING LOSSES AS REQ.
10 MIN.
HOT START EXHAUST TEST
7 MIN. MAX.
HOT SOAK ENCLOSURE TEST
END

Figure 7. Vehicle emissions test sequence.

the case, as shown by the first and tenth lines of Table 6. The middle of the FTP is a warmed-up, stop-and-go cycle and the catalysis is more effective in these conditions as shown in the bag 2 results in line two of Table 6. The whole FTP results shown in line three indicate that the Volare, at 37,000 miles, did not meet the tailpipe HC emissions standard for this year's model (1.5 g/mi); it did meet the NO_x standard (4.0 g/mi).

On day 1, the FTP was immediately followed by a one-hour SHED test for hot soak evaporative emissions.

After the one-hour cooldown in the SHED test, the NYCC was run. In this test the car is started hot, is driven in a stop and go manner at higher accelerations than in the FTP but at lower average speed of 7 mph. The NO_x emissions in this test were similar to the middle of the FTP, but the HC are 50% higher, most likely caused by more deceleration in the test.

After the NYCC test was completed, the CUE and steady state tests were run. The steady-state cruise tests gave the lowest HC-to-NO_x ratios mainly because of the lower HC emissions.

The car's diurnal evaporative losses were determined by standing over night in the SHED test. When converted to an equivalent number of grams per mile, the evaporative losses were well within the 1.5 g/mi standard for 1979 cars.

In terms of conditions suitable for reactivity assessments in smog chambers, only the high idle test or the cold start section of the FTP appear to have had reasonable HC-to-NO_x ratios.

Cryocondenser Methods

Need for Cryocondensers

Because of the distance separating the EPA dynamometer facility and the UNC chambers, a reliable method was needed to transport significant quantities of exhaust samples from one location to the other. To utilize exhaust samples from dynamometer tests in the UNC chambers, exhaust would have to be transported to the site for chamber injection; if direct injection from a vehicle was used at the site, then a smaller sample of the injected exhaust would have to be transported to

Table 6. Example of Dynamometer Test

(1979 Plymouth Volare 225/6-Cyl/2 BL/CAT

	HC		NO_x		CO		HC/NO_x
Test	ppmC	g/mi	ppmC	g/mi	ppmC	g/mi	
Day 1, FTP, cold start, 505s.	2507	3.62	992	3.9	22,922	66.7	2.72
Day 1, FTP, bag 2	1166	1.77	577	2.6	12,542	38.6	2.02
Day 1, FTP, all bags	1566	2.11	750	3.1	15,906	44.0	2.08
Day 1, NYCC # 1	1620	5.38	593	5.7	15,422	103.6	2.73
Day 1, CUE	1490	1.51	960	2.9	17,595	35.9	1.55
Day 1, SS-30 MPH	343	0.22	588	1.24	1,220	1.6	0.58
Day 1, SS-50 MPH	1445	1.20	1491	3.98	13,924	23.4	0.97
Day 1, Low Idle	126		92		88		1.37
Day 1, High Idle	1257		464		13932		2.71
Day 2, FTP, cold start, 505s.	2282	3.36	969	4.2	21,309	63.3	2.36
Day 2, FTP, all bags		2.04		3.3		44.0	
Day 2, NYCC # 2	1598	5.38	516	5.23		102.5	3.1

MSERB/EPA for detailed HC speciation for comparison with the dynamometer HC speciation data.

The large volume of a chamber side (150 m^3) and tailpipe concentrations of ≈2000 ppmC required large volumes (60–100 liters) of undiluted exhaust to achieve the desired 0.5 to 4.0 ppmC of nonmethane hydrocarbon (NMHC) in the chamber. Bags and pressurized tanks were considered impractical transport methods because of the volume needed and because of potential contamination and loss problems. Freezeout techniques to trap the hydrocarbons had been tried by Heuss *et al.*[21,22] with varying degrees of success. This technique involved significant sample modification and destructive techniques and therefore was impractical to use. A whole sample technique similar to that described by Rasmussen[23] was selected instead.

Description of Cryocondensers

Figure 8 shows the UNC cryocondenser used for the exhaust tests. Two different sizes of cylinders were used: a Hoke model 8HD3000, 3-liter, 1800 psi static tested, DOT-certified stainless steel sampling cylinder weighing 7.6 kg; and a Hoke 8LD3000, 3-liter, 400 psi static tested, DOT-certified stainless steel sampling cylinder weighing 4.0 kg. If a 200-liter air sample that had been condensed in the sample cylinders were allowed to fully evaporate, a 66-atmosphere pressure condition (≈1000 psi) would result. Because the cryocondensers are removed from the liquid nitrogen to allow the sample to be re-evaporated into the chambers, proper venting of the cryocondensers was critical to the safety of the operators. Both cylinders were therefore equipped with safety devices including: both a pressure gauge and a vacuum gauge to monitor the internal pressure condition; a rupture disk, calibrated to rupture at least a one-cm diameter hole if the internal pressure exceeded 200 psi; and a pressure release valve calibrated to let the cryocondenser contents vent if the pressure exceeded 150 psi.

Principle of Operation

In use, the cryocondenser was initially evacuated, immersed in a 5-liter dewar filled with liquid nitrogen (LN_2), and the inlet valve opened. The initial vacuum drew in air. The 3°C temperature difference between liquid air (−193°C) and liquid nitrogen (−196°C) and the efficient heat transfer provided by the large area of the walls condensed the entering air. The liquid air (including the trace contaminants) was collected in the bottom of the cylinder. This total condensation of the air sample maintained the initial vacuum. All of the air that entered the crycondenser was

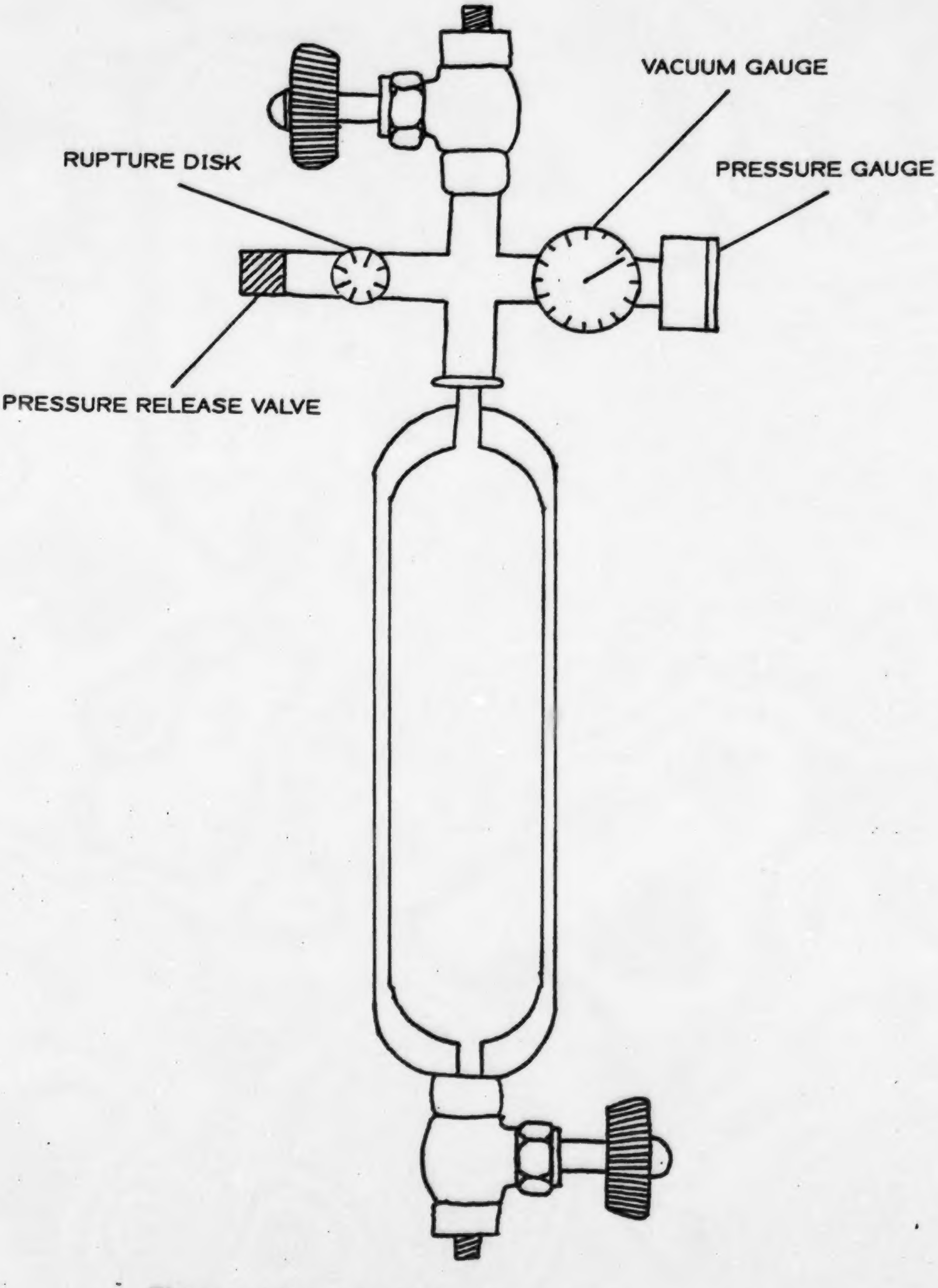

VACUUM GAUGE
RUPTURE DISK
PRESSURE GAUGE
PRESSURE RELEASE VALVE

Figure 8. UNC cryocondenser equipped with pressure and vacuum gauges, rupture disk, and pressure release valve.

condensed and the sampling vacuum of the cryocondenser was therefore sustained for long periods (hours at low sample rates) provided that the LN_2 supply was maintained.

The larger, high-pressure cryocondenser required large amounts of LN_2 to lower its temperature. During sampling introduction into the chamber, this cylinder required more than 10 minutes of heating with a hot air gun just to melt the ice off the outside. This large cylinder, because of its high thermal stability, was good for long term storage and for transporting exhaust samples to remote locations. Because of its smaller mass, the 400-psi, smaller cylinder could be cooled much faster with less LN_2. The 400-psi cylinder was able to condense exhaust at 6–7 liters/minute for more than 30 minutes, and required only 5 minutes to heat to the point of melting the frozen water collected inside the sample cylinder. The 400-psi cylinder was used for all subsequent tests.

Cryocondenser Tests with Exhaust

Initial tests of sample collection rate, total volume collected, and sample stability for the cryocondenser were performed using exhaust from a 1981 Chevrolet Luv truck. No sampling difficulties were encountered in these tests. In later tests using the 1979 Plymouth Volare and the 1972 Dodge Charger at the EPA dynamometer facility, the cryocondenser stopped drawing sample after four minutes of sampling. The Chevrolet truck used an "air pump injection" system to reduce tailpipe emissions and thus had a near ambient level of oxygen in the tailpipe. The 79 Plymouth was equipped with a catalytic system and the Dodge had a non-catalytic, straight exhaust system. Both cars were expected to produce an exhaust low in oxygen.

A series of bag tests using mixture compositions ranging from 100% nitrogen to 20% oxygen/80% nitrogen demonstrated that sufficient oxygen was needed to raise the boiling point of the condensed liquid "air" to be above that of LN_2. This temperature difference between liquid air and liquid nitrogen was needed for the cryocondenser to condense the entering sample and thus to continue to draw sample for more than a minute. A sampling inlet system that blended $\approx$1.5 liter/minute of tank oxygen into the sample stream was constructed. With this arrangement, the cryocondenser could sample exhaust from the Plymouth at 6 liters/minute for more than 30 minutes.

Chamber Injection Methods

Two types of injections were performed. The first was a direct injection of exhaust from a running automobile into both chambers simultaneously. The second was a direct injection of exhaust in one chamber side while a sample with the cryocondenser was simultaneously collected. The cryocondenser's contents were subsequently evaporated into the other chamber side.

The initial purpose of the direct injections at the site was to confirm that the reactivities of the cryocondenser-injected-sample and the directly-injected-sample were the same. This required that identical samples be injected into both the chamber and the cryocondensor. The temporal uniformity of the exhaust sample composition was of concern because as long as 30 minutes was required to inject the desired concentration sample into both chambers.

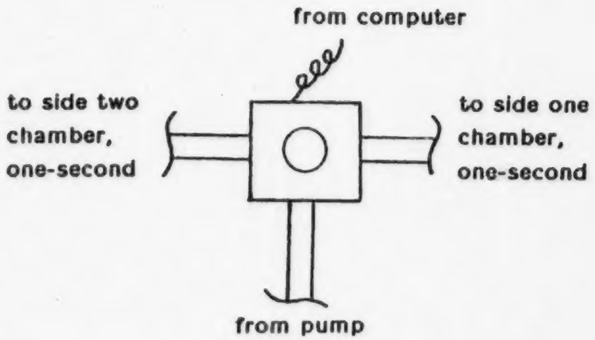
At the chamber site, a constant 2800 RPM, high idle was used to provide exhaust for the injection. This was one of the reasons for including the high idle tests in the MSERB/EPA dynamometer tests.

Direct Exhaust Injection Methods

Two different injection systems were used and are shown in Figure 9. In both cases a stainless steel sample inlet was placed inside the tailpipe of the car and an exhaust sample was drawn by a large stainless steel, metal bellows pump at between 12 and 14 liters/minute. A 4-cm diameter Teflon-coated, glass-fiber filter was used to remove particulates to protect the metal bellows pump flutter valves.

In the case of the direct-direct injection, the pump outlet went to a Teflon two-way valve that was computer controlled to be open to one side of the chamber for 1-second and then the other side for 1-second. This oscillation between the two chamber sides compensated for temporal variations in the emission rates and hydrocarbon composition.

In the case of the cryocondenser-direct injection, the pump outlet went to a tee which fed two matched glass capillaries for controlling flow. One capillary went to the chamber and one capillary went to the cryocondenser inlet. The capillaries were selected to have a flowrate less than the cryocondenser self-sampling-rate so that they would control the flow, not the cryocondenser. In the case of the cryocondenser-direct injection tests, oxygen was fed to the sample stream at about a)direct–direct injection system


from computer
to side two
chamber,
one-second
to side one
chamber,
one-second
from pump

b)cryocondenser–direct injection system

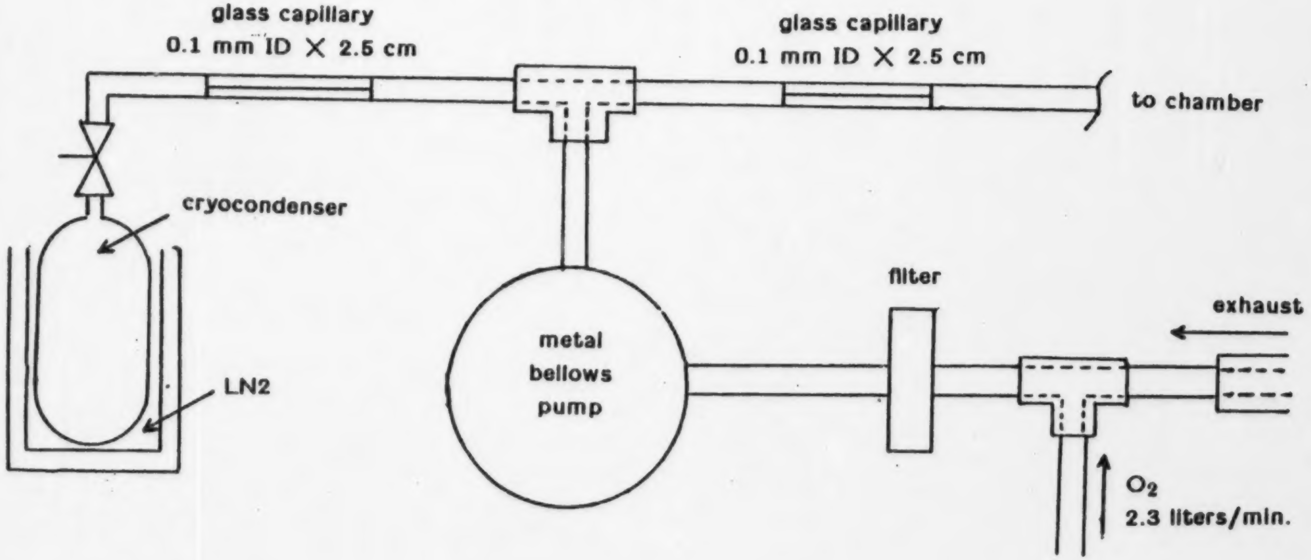

glass capillary
0.1 mm ID × 2.5 cm
glass capillary
0.1 mm ID × 2.5 cm
to chamber
cryocondenser
LN2
metal
bellows
pump
filter
exhaust
O_2
2.3 liters/min.

Figure 9. UNC outdoor smog chamber automobile exhaust injection systems.

2-liters/minute to allow the cryocondenser to function. Since the stream was split after the oxygen addition, both the chamber and the cryocondenser received the same sample composition.

The protocol used for performing direct injection auto exhaust tests called for the vehicle or vehicles to be tested to be brought to the research site on the day before the scheduled experiment, and backed into position next to the chambers. The morning of the experiment the stainless steel sample line was inserted into the tailpipe of the vehicles.

To prepare the automobile for the injection, the hood was opened, and a electronic tachometer was connected to monitor the RPM. Then the throttle preset cam on the carburetor was set between the first and second notches on the cam. This set the vehicle for a 2500-2800 RPM high idle once the engine had warmed up for a few minutes. To start the injection, the key was simply turned in the ignition. (The carburetor had been primed while getting the throttle preset cam into position.) Before starting the pump to inject into the chamber, the car was allowed to come up to idle, which generally took two to three minutes. This could be observed on the tachometer. Actual injection usually started two and a half minutes after starting the engine.

Chamber injections were monitored on the NO_x meter, the Beckman 6800 NMHC analyzer, and on the THC valve on the Carle I GC (see examples in Appendix B). Each of these instruments was set up to record only on the side into which the injection was taking place. The Beckman 6800 was set for a five-minute cycle time, and data from the Carle I GC was obtained approximately every two minutes. The hydrocarbon to NO_x ratio was continuously monitored. In the case that the vehicle was producing a very low HC-to-NO_x ratio, the injection pump was stopped and the vehicle was set up once again.

Cryocondenser Injection Methods

In making cryocondenser injections, the following procedure was used. As the cryocondenser warmed, the internal pressure increased due to evaporation of low boiling point hydrocarbons and material was driven out of the open intake (now an outlet). The attached gauges were monitored to assure that the pressure build-up remained at a safe level. Re-immersion in LN_2 was sometimes used to slow down the pressure build up, but this technique was not generally used.

When the internal pressure had decreased to below 2 psi, the cryocondenser was heated with a hot air gun until all the ice on the outside of the cylinder had melted. The cryocondenser then had liquid water inside from the exhaust. The water was drained out the bottom tap into a glass impinger. It generally had a deep yellow color, a strong odor, and a pH of 1-2. The water in the impinger was separately heated and injected into the chamber using a clean air stream. The NO_x in the chamber increased 10-20% during the evaporation of this water.

Meanwhile, the cryocondenser was placed in a specially built, low temperature "tube heater" and about 50-liters of ambient air were purged through the cryocondenser using a Teflon lined diaphragm pump while the cylinder was heated slowly to about 100° C.

Some of the sample NO was thermally oxidized to NO_2 by this injection process and "touch-up" injections from tanks of NO and NO_2 were used to balance the two chambers in total NO_x and in NO_2-to-NO ratios.

Two Gasolines, One Car Injection Methods

Experiments testing one car, one operating mode, and two gasolines used the Dodge Charger. The fuel line to the carburetor on this vehicle was modified to put a three way valve immediately before the carburetor. Each fuel line had its own fuel filter.

The basic protocol for these experiments was essentially the same as that used for the direct injection of exhaust. After setting up the vehicle and injecting to the target concentration in the first chamber, the Teflon tubing from the metal bellows pump was removed from the chamber, and the pump was turned off. The tubing was then inserted into the second chamber. At this same time, the three-way valve was turned to its alternate position, and the carburetor would begin getting fuel from an external source of gasoline.

Before turning the metal bellows pump on again to inject into the second chamber, the vehicle was allowed to run for five minutes, to give the new fuel time to displace the old fuel in the carburetor. (This time was arrived at by changing the three-way valve when no fuel was available on the alternate fuel line, and waiting until the engine stopped.)

For the injection into the second chamber, the goal was to match the THC concentration achieved in the first chamber. Once this goal was met, the NO_x concentrations were matched by manual tank injections of NO_2 and NO.

Two Cars Injection Methods

The protocol for experiments which used exhaust from two cars was similar to the protocol used for one car with two gasolines. Both vehicles were brought to the research site the afternoon before the experiment and left overnight, so that both vehicles could be run from a cold start. The injection system using the high-volume metal bellows pump and the teflon tubing was set up as described earlier. Exhaust from the Plymouth Volare was injected first because we frequently encountered problems obtaining resonable HC concentrations and HC-to-NO_x ratios from this vehicle.

After setting up the vehicle and injecting to the target concentration in the first chamber, the Teflon tubing from the metal bellows pump was removed from the chamber. The pump inlet was also removed from the first vehicle's tailpipe. The pump was allowed to run for a few minutes to remove the last of the exhaust from the pump lines. The stainless tube would then be put into the tailpipe of the second vehicle, and the outlet Teflon tubing was inserted into the second chamber. The second vehicle was started and allowed to warm up for about three minutes. The metal bellows pump was then turned on, and the injection started. For the injection into the second chamber, the goal was to match the THC concentration achieved in the first chamber. Once this goal was met, the NO_x concentrations were matched by manual tank injections of NO_2 and NO if needed.

Synthetic Mixture Injection Methods

Hydrocarbon data from four gas chromatographs covering the range from CH_4 to C_{12} were used to determine the composition of exhaust from the vehicles used in this study. A list (shown in Table 7) of the most important compounds in terms of both mass and compound-class type was prepared. Although benzene is considered unreactive, its non-negligible reactivity and its prominence in exhaust led us to include it in the synthetic mixture. Acetylene, another "non-reactive" and a major component of exhaust was not included, however. Analysis for oxygenates using the DNPH method showed that formaldehyde was by far the most prominent aldehyde. Formaldehyde was used to represent all the aldehydes in the exhaust.

Table 7. Composition of Synthetic Automobile Exhaust
(Units are Carbon Fraction)

Compound	Fraction
butane	0.0391
isopentane	0.0519
2,2,4-trimethylpentane	0.1121
ethylene	0.2391
propylene	0.0416
1-butene	0.0196
t-2-butene	0.0196
benzene	0.0538
toluene	0.2115
m-xylene	0.1026
o-xylene	0.0481
1,2,4-trimethylbenzene	0.0564
formaldehyde	0.0200

The compounds which existed as liquid at room temperature were mixed and refrigerated. This liquid was injected as a single mixture with the corresponding gaseous components to achieve the correct final composition. Isopentane was injected separately from a chilled (dry ice) syringe as a liquid. The gaseous compounds were injected from individual tanks. Flow rates were checked and adjusted immediately before injection. Injection of formaldehyde was accomplished by heating paraformaldehyde in a U-tube heated with an electric hot air blower while the tube was purged with very dry "zero air".

5

Results

Supporting Data

Dynamometer Tests

Tests Performed

Dynamometer tests were performed on both cars in June of 1982, October of 1983, and March of 1984.

In the June, 1982 tests, both cars had a complete series of tests on two consecutive days: FTP, Hot soak evaporative, NYCC, CUE, steady state cruise, idle, and diurnal soak evaporative tests, FTP on the second day and NYCC on the second day. In each of the FTP tests, three HC sample bags, one in each part of the cycle, were collected for detail HC speciation by GC. In the NYCC, CUE, SS, and idle tests, one bag each was collected throughout the entire cycle. Altogether thirteen sample bags for each car were collected and analyzed by GC. In addition, UNC personnel operated the cryocondensers in selected tests and these were subsequently evaporated into bags for analysis along with the standard sample bags.

In the October 1983 tests, only the FTP, NYCC, and high idle tests were performed. In August, the Plymouth's carburetor had been badly mis-adjusted by university service mechanics (remember that this car was owned and serviced by the University). In the initial dynamometer tests at MSERB, the car performed very poorly. MSERB, at our request, first readjusted the car and re-ran the tests.

The car's performance was essentially the same as the 1982 tests. After further discussion, Dr. Bradow suggested that MSERB replace the mis-adjusted carburetor with a new factory one. After the replacement, the car was tested in the FTP, NYCC, and High Idle cycles. Bag samples for detailed HC analysis were collected in the three parts of the FTP, and one each in the NYCC and Idle tests. The car's NO_x performance was better than its first 1983 test, but HC emissions were worse than the re-tuned tests before the carburetor was replaced.

In the October 1983 tests, the Dodge Charger was tested on the dynamometer in the FTP, NYCC, and High Idle. No sample bags were collected for detailed HC analysis in these test, however.

In the March 1984 tests, both cars were run in the FTP and High Idle tests. Cryocondenser samples were drawn for detailed HC analysis on UNC's gas chromatographs, especially the new Sigma 2 capillary system (see Appendix B for description of this system). In addition, a bag was prepared from the cryocondenser for MSERB analysis so that the two analyses could be compared. Finally, a "cold" start, High Idle cryocondensor sample was drawn at the site using identical techniques to a direct chamber injection. This sample was analyzed by both MSERB and UNC.

Dynamometer Mass Emissions Results

Table 8 and Table 9 show selected results from the 1982 dynamometer tests for the 1979 Plymouth Volare and the 1970 Dodge Charger. The actual tailpipe concentrations of hydrocarbon and oxides of nitrogen varies much less from driving cycle to driving cycle than did the trip or per mile emissions. This is because the speeds differ so much between cycles.

The emissions standards for 1972-1974 automobiles were: 3.4 g/mi hydrocarbons, 4.4 g/mi oxides of nitrogen and 39 g/mi carbon monoxide. Preliminary MSERB/EPA data from the 46-car VOC study[16] indicates that the average and range of average results for model years 1975 to 1981 (50% of the cars were 1980 or newer) were (in g/mi):

Species	average FTP	±2 s.d. FTP	average NYCC	±2 s.d. NYCC
HC	1.4	0.6—3.4	4.8	2.4—11
NO_x	2.2	1.1—2.2	3.3	1.9—3.4
CO	16.3	8—32	46.9	30—92

The 1972 Dodge did fairly well on the HC tests, but was a poor performer on the NO_x and CO tests relative to the newer cars. The 1979 Plymouth Volare missed its certification HC-emission standard of 1.5 g/mi by 0.5 g/mi; so did a lot of cars in the 46-car VOC study. The 1982 dynamometer data for the Plymouth Volare were included in the VOC study data for 1979 cars. There were four other cars tested in the VOC study. The FTP average results for all five 1979 cars were (units are g/mi):

Model	CO	NO_x	HC
Chevette	27	0.9	1.23
Mazda	5	1.8	1.25
Toyota	16	2.0	1.58
Volare	44	3.2	2.08
Ford	8	3.1	2.22

The large cars seemed to be poor performers compared to the small cars.

Table 6 showed that most of the emissions in the FTP for the Volare came from the cold start and that the middle part of the cycle, with catalysis warmed up, was 33% below the certification standard (1.0 g/mi vs. 1.5 g/mi). Like the Dodge, the Volare was a relatively poor performer on NO_x and CO emissions.

Table 10 and Table 11 show selected results from the 1983 dynamometer tests. Even after the new carburetor had been replaced, the Volare exceeded the HC-emissions standard by a factor of two; and was 33% higher than it was in its first test in 1982. The majority of the emissions in the FTP, however, were in the cold start portion of the test and after the catalysis warmed up, the emissions dropped to a low value.

The Dodge Charger tests showed that this car actually improved its performance. Because the car was not being driven routinely, this finding was a little surprising.

Cryocondenser Dynamometer HC Composition Tests

The UNC cryocondenser was used to collect exhaust directly from the tailpipe while the cars were undergoing dynamometer tests at MSERB/EPA and the samples were subsequently evaporated into their standard bags for detailed hydrocarbon analysis at MSERB/EPA. The concentrations in the cryocondenser bags were much higher than those in the regular test bags because the latter had a 12-17 fold dilution from the constant volume sampling system on the dynamometer. The cryocondenser bags were subsequently diluted by a factor of 10 before analysis.

The samples collected during the dynamometer tests and the samples from evaporating the cryocondenser into a bag were analyzed by MSERB/EPA using gas chromatography to provide hydrocarbon speciation and quan tification. The gas chromatographic method was a two column analytical scheme.[16]

The low molecular weight C_1 to C_3 hydrocarbons were separated on an 0.32-cm dual-bed packed column of Poropak QS followed by a silica-gel column to separate methane. The C_4 to C_{12} hydrocarbons were separated on a F50 Versilube WCOT stainless steel capillary column. The first column was operated isothermally at room temperature and the second column was programmed from -45° to 85°C after the initial injection at -95°C.

While MSERB analyzed the bags, UNC began a GC/MS study of the cryocondenser performance using exhaust collected in both bags and cryocondensers from idle-mode operation of the Dodge Charger in the School of Public Health parking lot near the mass spectrometer laboratory. A major goal was to calibrate the Carlo Erba capillary column gas chromatograph, located at the school laboratory, for exhaust analysis using the same columns as used in the GC/MS analysis. The GC/MS analyses were performed on the Department of Environmental Sciences' VG Micromass 70/70 double-focusing mass spectrometer. Compounds were identified by comparing their spectra against those from spectra libraries as well as by direct comparison to standards on the same GC/MS instrument. Eventually, very detailed gas chromatograms of exhaust with high resolution mass spectrum identifications of more than 90 peaks were produced. Examples of chromatograms and mass spectra are given in Appendix B.

Table 8.

Emissions During 1982 Dynamometer Tests of 1979 Plymouth Volare Using Different Driving Modes

Emissions :

Item	FTP1	FTP2	NYC1	NYC2	IDLE
HC :					
g/mi	2.10	2.04	5.38	5.38	0.67
ppmC	1566	1473	1599	1621	1257
NOx :					
g/mi	3.11	3.36	5.23	5.67	0.78
ppm	750	780	516	571	465
CO :					
g/mi	44.1	44.1	107.5	103.6	14.96
ppm	15902	15441	15820	15446	13932
HC/NOX Ratio :					
	2.1	1.9	3.1	2.8	2.7

FTP1,FTP2 — Federal Test Procedure day 1 and day 2; NYC1,NYC2 — New York City Cycle day 1 and day 2; IDLE — 2800 RPM idle, g-min^{-1}.

Table 9.

Emissions During 1982 Dynamometer Tests of 1972 Dodge Charger Using Different Driving Modes

Emissions :

Item	**FTP1**	**FTP2**	**NYC1**	**NYC2**	**IDLE**
HC :					
g/mi	4.75	4.40	7.99	7.86	0.408
ppmC	2,940	2,662	2,075	2,167	1,245
NOx :					
g/mi	3.10	3.08	5.38	6.31	0.072
ppm	499	497	428	500	63
CO :					
g/mi	102.90	105.30	144.70	161.20	7.95
ppm	31,121	31,453	18,609	22,011	11,999
HC/NOX Ratio :					
	5.9	5.4	4.8	4.3	19.8

FTP1,FTP2 — Federal Test Procedure day 1 and day 2; NYC1,NYC2 — New York City Cycle day 1 and day 2; IDLE — 2800 RPM idle, g-min^{-1}.

Table 10.
Emissions During 1983 Dynamometer Tests of 1979 Plymouth Volare Using Different Driving Modes

Test :	**FTP**	**NYC**	**IDLE**
Emissions :			
HC :			
g/mi	3.59	22.27	0.19
ppmC	3,203	7,342	743
NOx :			
g/mi	3.67	5.09	0.29
ppm	805	450	306
CO :			
g/mi	49.0	203.7	0.42
ppm	21,042	33,270	816
HC/NO_x Ratio :			
	4.0	16.3	2.4

FTP — Federal Test Procedure
NYC — New York City Cycle
IDLE — 2800 RPM idle, g-min^{-1}

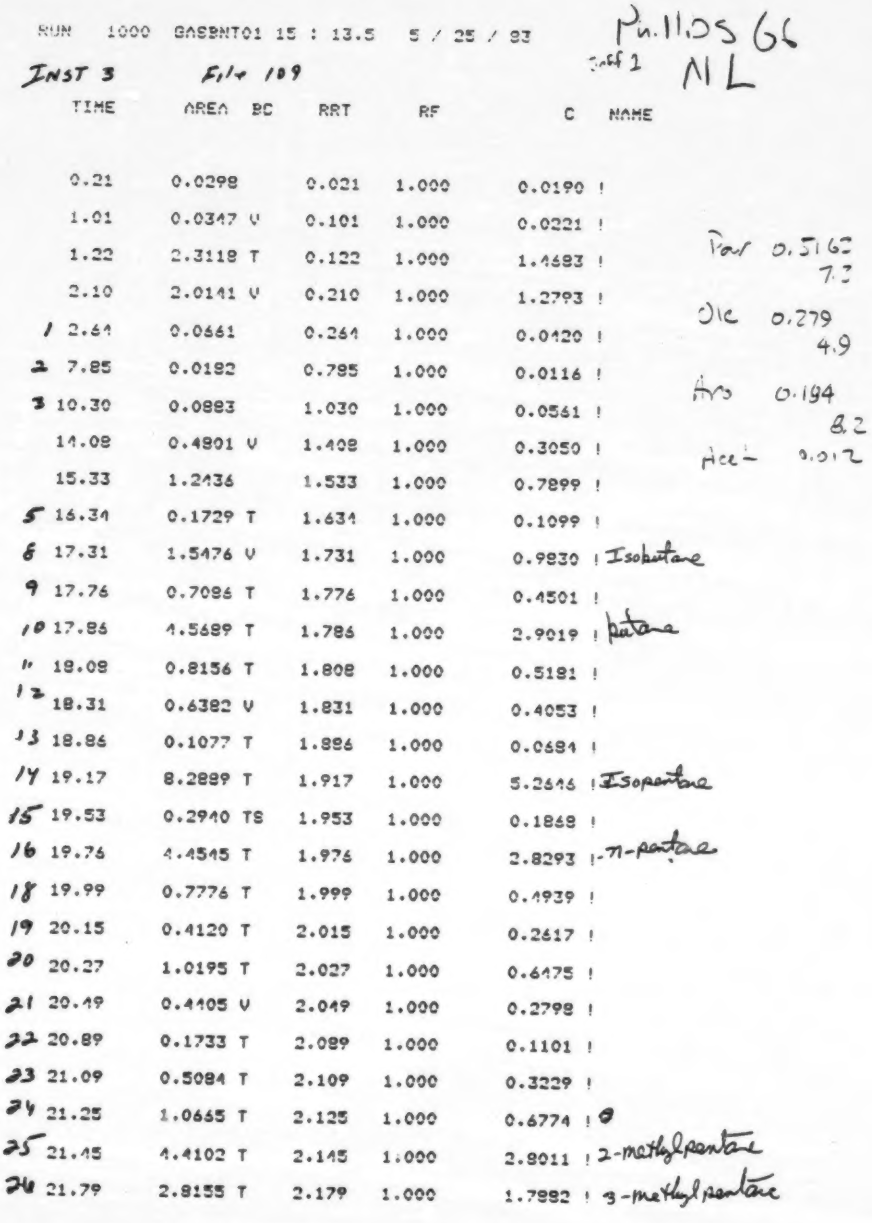
Table 11.

Emissions During 1983 Dynamometer Tests of 1972 Dodge Charger Using Different Driving Modes

Test :	**FTP**	**NYC**	**IDLE**
Emissions :			
HC :			
g/mi	3.57	5.46	0.31
ppmC	2,424	1,780	802
NOx :			
g/mi	4.00	5.98	0.14
ppm	782	595	113
CO :			
g/mi	66.0	86.6	7.2
ppm	21,802	13,982	9,212
HC/NO$_x$ Ratio :			
	3.1	3.0	7.1

FTP — Federal Test Procedure
NYC — New York City Cycle
IDLE — 2800 RPM idle, g-min^{-1}

The HC species data for all the bags and for the gasolines used in the tests were received from MSERB initially as computer generated lists of ppmC for each species. We subsequently requested data as raw areas for each test and a species peak-identification list. An example of such a MSERB data list is shown in Figure 10 and the species identification list is given in Table 12.



Phillips 66
Duff 1 ML

```
   RUN   1000  GASBNT01 15 : 13.5   5 / 25 / 83
INST 3        File 109
      TIME       AREA  BC    RRT      RF            C    NAME

      0.21     0.0298       0.021   1.000       0.0190 !
      1.01     0.0347 V     0.101   1.000       0.0221 !
      1.22     2.3118 T     0.122   1.000       1.4683 !
      2.10     2.0141 V     0.210   1.000       1.2793 !
   1  2.64     0.0661       0.264   1.000       0.0420 !
   2  7.85     0.0182       0.785   1.000       0.0116 !
   3 10.30     0.0883       1.030   1.000       0.0561 !
     14.08     0.4801 V     1.408   1.000       0.3050 !
     15.33     1.2436       1.533   1.000       0.7899 !
   5 16.34     0.1729 T     1.634   1.000       0.1099 !
   6 17.31     1.5476 V     1.731   1.000       0.9830 ! Isobutane
   9 17.76     0.7086 T     1.776   1.000       0.4501 !
  10 17.86     4.5689 T     1.786   1.000       2.9019 ! butane
  11 18.08     0.8156 T     1.808   1.000       0.5181 !
  12 18.31     0.6382 V     1.831   1.000       0.4053 !
  13 18.86     0.1077 T     1.886   1.000       0.0684 !
  14 19.17     8.2889 T     1.917   1.000       5.2646 ! Isopentane
  15 19.53     0.2940 TS    1.953   1.000       0.1868 !
  16 19.76     4.4545 T     1.976   1.000       2.8293 ! n-pentane
  18 19.99     0.7776 T     1.999   1.000       0.4939 !
  19 20.15     0.4120 T     2.015   1.000       0.2617 !
  20 20.27     1.0195 T     2.027   1.000       0.6475 !
  21 20.49     0.4405 V     2.049   1.000       0.2798 !
  22 20.89     0.1733 T     2.089   1.000       0.1101 !
  23 21.09     0.5084 T     2.109   1.000       0.3229 !
  24 21.25     1.0665 T     2.125   1.000       0.6774 ! θ
  25 21.45     4.4102 T     2.145   1.000       2.8011 ! 2-methylpentane
  26 21.79     2.8155 T     2.179   1.000       1.7882 ! 3-methylpentane
```

Par 0.5162
7.3
Olc 0.279
4.9
Aro 0.194
8.2
Acet 0.012

Figure 10. Example of MSB Hydrocarbon Analysis Raw Data List.

Table 12. MSERB Species Identification List

1: METHANE
2: ETHYLENE
3: ETHANE
4: ACETYLENE
5: PROPYLENE/ PROPANE
6: PROPADIENE
7: METHYL ACETYLENE
8: ISOBUTANE
9: BUTENE-1/ ISOBUTYLENE
10: N-BUTANE/ 1,3-BUTADIENE
11: TRANS-2-BUTENE
12: CIS-2-BUTENE
13: 3-METHYL-1-BUTENE
14: ISOPENTANE
15: PENTENE-1
16: N-PENTANE/ 2-METHYL-1-BUTENE
17: 2-METHYL-1,3-BUTADIENE
18: TRANS-2-PENTENE
19: CIS-2-PENTENE
20: PENTYNE
21: 2 METHYL-2-BUTENE
22: CYCLOPENTENE
23: CYCLOPENTANE/ 3-METHYL-1-PENTENE
24: 2,3-DIMETHYLBUTANE
25: 2-METHYLPENTANE/ 2,3-DIMETHYL-1-BUTENE
26: 3-METHYLPENTANE
27: 1-HEXENE/ 2-ETHYL-1-BUTENE
28: N-HEXANE/ CIS-3-HEXENE
29: 2-METHYL-2-PENTENE
30: CIS-2-HEXENE
31: HEXYNE
32: METHYLCYCLOPENTANE/ 3-METHYLTRANS-2-PENTENE
33: 2,4-DIMETHYLPENTANE
34: METHYLCYCLOPENTENE
35: BENZENE/ CYCLOHEXANE
36: CYCLOHEXENE/ 2,3-DIMETHYLPENTANE/ 2-METHYLHEXANE
37: 3-METHYLHEXANE
38: 2,2,4-TRIMETHYLPENTANE
39: N-HEPTANE
40: 2,4,4-TRIMETHYL-1-PENTENE/ 3-METHYLHEXANE
41: METHYLCYCLOHEXANE
42: 1-CIS-4-DIMETHYL CYCLOHEXANE
43: 2,4 & 2,5-DIMETHYLHEXANE
44: 2,3,4-TRIMETHYLPENTANE
45: 2,3,3-TRIMETHYLPENTANE
46: TOLUENE/ 2,3-DIMETHYLHEXANE
47: 2-METHYLHEPTANE
48: 4-METHYLHEPTANE
49: 3-METHYLHEPTANE
50: 2,2,5-TRIMETHYLHEXANE
51: N-OCTANE
52: 2,3,5-TRIMETHYLHEXANE
53: 2,4-DIMETHYLHEPTANE
54: 2,5 & 3,5-DIMETHYLHEPTANE
55: ETHYLBENZENE/ 2,3-DIMETHYLHEPTANE
56: P&M-XYLENE
57: 4-METHYLOCTANE
58: 3-METHYLOCTANE
59: O-XYLENE/ UNK C9 PARAFFIN
60: 2-METHYLOCTANE
61: TRANS-2-NONENE
62: NONANE
63: N-PROPYLBENZENE
64: 1,3,5-TRIMETHYLBENZENE
65: 2,3-DIMETHYLOCTANE
66: METHYL CYCLOOCTANE
67: CIS-PROPYLBENZENE
68: 1,2,4-TRIMETHYLBENZENE
69: SECBUTYLBENZENE
70: N-DECANE
71: 1,2,3-TRIMETHYLBENZENE
72: INDANE
73: 4-PHENYL-1-BUTENE
74: 1-METHYL-3N-PROPYLBENZENE
75: 1,3-DIETHYLBENZENE
76: N-BUTYLBENZENE
77: 1,2-DIETHYLBENZENE
78: 2-METHYLDECANE
79: CYCLOPENTYLCYCLOPENTANE
80: 1-UNDECENE
81: N-UNDECANE
82: TRANS-1-PHENYLBUTENE-1
83: UNKNOWNS

MSERB GC Data Treatment

In attempting to enter the MSERB species data into the UNC hydrocarbon compositional analysis program (ANALYZHC) used to compute HC class fractions, we encountered some difficulties. There were relatively high concentration compounds identified in the MSERB analysis that were not identified in any of our analyses. There were relatively high concentration compounds identified in our GC/MS analysis that were not identified in the MSERB analyses. Also there were a large number of compounds in the MSERB analysis that were not resolved, whereas, for the most part, these were resolved in our analysis.

The compounds that were identified in the MSERB analyses that were not identified in any of our analyses were:

- methyl-cyclo-octane
- 4-phenyl-1-butene
- cyclo-pentyl-cyclopentane
- trans-1-phenyl-butene-1

The compounds that were identified in our GC/MS analyses that were not identified in the MSERB analyses were:

- styrene
- o-, p-, m-ethyl-toluene
- methyl-indane
- naphthalene
- methyl-naphthalenes

Discussions with MSERB personnel indicated that the species identifications in their data were "preliminary" and that the identifications were being further investigated. MSERB had no pure standards or other calibration sources available for the compounds that they had identified as above. In addition, physical data, such as boiling points for some of these compounds could not be found. As will be shown below, these compounds identified by MSERB appeared among the top 20 compounds in the exhaust, with some among the top 10 compounds, so it was important to reconcile the data.

Based on our GC/MS work on the same gasoline and exhaust and the relative patterns in the two datasets, we determined that at least five compounds had probably been mis-identified by MSERB. For example, our GC/MS work clearly showed that naphthalene was a significant species in exhaust (see specta in Appendix B). A comparison of our relative retention data with their relative retention data showed that MSERB was most likely identifying the naphthalene peak as cyclo-pentyl-cyclopentane.

Similar review and comparison suggested that at least four other compounds were likely mis-identified in the MSERB data. These were subsequently changed by us in our processing of MSERB's data as follows:

- methyl-cyclooctane changed to o-ethyl-toluene
- 2,3-dimethyl-octane changed to 1,3,5-trimethyl-benzene
- 1,3,5-trimethyl-benzene changed to m-ethyl-toluene
- cyclo-pentyl-cyclopentane changed to naphthalene
- 2-methy-decane changed to methyl-naphthalene

Although we believed that there were other mis-identifications in the MSERB data, we did not change any other identifications. The five changes above brough about approximately an 8% shift of carbon into the aromatics class for most samples.

After this report was written, MSERB changed the species identifications in the VOC study appendices.[16] Appendix C of this report, Selected Data Tables, includes a comparison of the original species identifications, the changes we made for this report, and the species identifications used by MSERB in the VOC study appendices.

One of the goals of this project was to provide modelers with a breakdown of the paraffin, olefin, and aromatic content of the initial NMHC content in the automobile exhaust used in the chamber runs. This would provide guidance on how the unspeciated HC in the injections should be entered into the models. The MSERB data were originally thought to satisfy this goal. In the MSERB analysis, however, a large number of paraffins and olefins or paraffins and aromatics were not separated, for example:

- butene-1/iso-butylene
- n-butane/1,3-butadiene
- n-pentane/2-methyl-1-butene
- cyclopentane/3-methyl-1-butene
- 2-methyl-pentane/2,3-dimethyl-butene
- n-hexane/cis-3-hexene
- cyclohexane/benzene
- 2,3-dimethyl-pentane/2-methyl-hexane/cyclohexene
- 2,3-dimethyl-hexane/toluene
- 2,3-dimethyl-heptane/ethyl-benzene
- unknown C_9 paraffin/o-xylene

In analyzing the data for our purposes, we have used our site data and our GC/MS data, in which many of the compounds were resolved, to estimate splitting factors for the MSERB data. We have applied these factors to the MSERB raw GC peak data to produce estimates for the individual species.

In addition, the nature of the first column utilized in the MSERB GC system makes the method prone to water interferences. This strongly affected the analysis of acetylene, ethylene, and propylene especially in the cryocondenser samples. With typical diluted dynamometer samples, the water vapor concentration was much lower and less of a problem existed. This water interference problem created some difficulties in the direct–crycondenser comparisons described below.

Finally, in the MSERB data processing, peak identification was done by a matching process between an analysis chromatogram with a standard gasoline chromatogram. For one analysis of exhaust for UNC in the 1982 data, a missing peak caused the results to be mismatched by one compound for most of the analysis leading to major changes in calculated composition. A subsequent re-matching among the data lists supplied by MSERB allowed us to correct the error. Not all samples from MSERB were subjected to this type of extensive analysis.

All MSERB/EPA data reported here have had the species identifications changed as described above, and the un-resolved peaks have been partitioned with UNC derived splitting factors into specific species. That is, we have changed the species identifications of five compounds and we have apportioned the concentration of each unresolved peak among the species listed as being unresolved in the peak. The latter step was performed for five to ten peaks.

The species identifications and the fractional carbon distributions for all MSERB GC analyses are listed in Appendix C. The term "MSB ANALYSIS, UNC IDS" is used to indicate that MSERB actually did the GC analysis and we changed the species identifications as described above. The term "UNC ANALYSIS, UNC IDS" means that we did both the GC analysis and assigned the species identifications.

Cryocondenser Performance

Figure 11 compares the two NYCC direct samples to the simultaneously collected cryocondenser samples from the 1982 MSERB dynamometer tests. In this figure, the MSERB assigned compound number was used to match the peaks for each data set pair; the concentrations reported in each data set were then used as the x and y values in the plot. The agreement of detailed composition even at the low concentration fractions is good for both comparisons. This clearly shows that the crycondenser sample was as good as a replicate analysis by standard bag techniques and further that, although MSERB may not have correctly identifed the peaks, they were generally consistent in assigning the same peak the same number.

The complexity and relative distribution of compounds in the exhaust sample are shown in Figure 12, which illustrates in a chromatogram-like manner the composition as a function of boiling point for the first NYCC direct sample from the 1982 dynamometer test (MSERB analysis, UNC identifications). This figure shows that, although there are more than 90 compounds detected, only about 25 compounds have a concentration above 1% of the total NMHC. In Table 13, the carbon percent of the top 21 compounds (those greater than about 1%) are compared for the two NYCC and the idle samples for both the directly measured and evaporated cryocondenser samples. The agreement between the direct and cryocondenser samples for the top 21 compounds in the exhaust is excellent. The detailed distribution of about two-thirds of the total hydrocarbon is within 3% between the direct samples and the evaporated cryocondenser samples.

Table 14 summarizes the hydrocarbon composition by class for the direct samples taken through the dynamometer dilution system and for evaporated cryocondenser tailpipe samples. The class agreement between a direct sample and the matching cryocondenser sample was as good as the agreement on repeating the direct tests. In addition, the operating modes appeared to have little effect on the class composition. The idle samples had fewer compounds identified. These also had lower paraffin fractions and larger unknown fractions. These results were caused by the low NMHC concentration in these samples: ≈40 ppmC compared to ≈160 ppmC in the other modes.

From these data we concluded that not only did the cryocondenser performs well as a sampler but also that the addition of oxygen to the cryocondenser to establish a condensing condition in the exhaust did not have a detectable effect on the hydrocarbon composition.

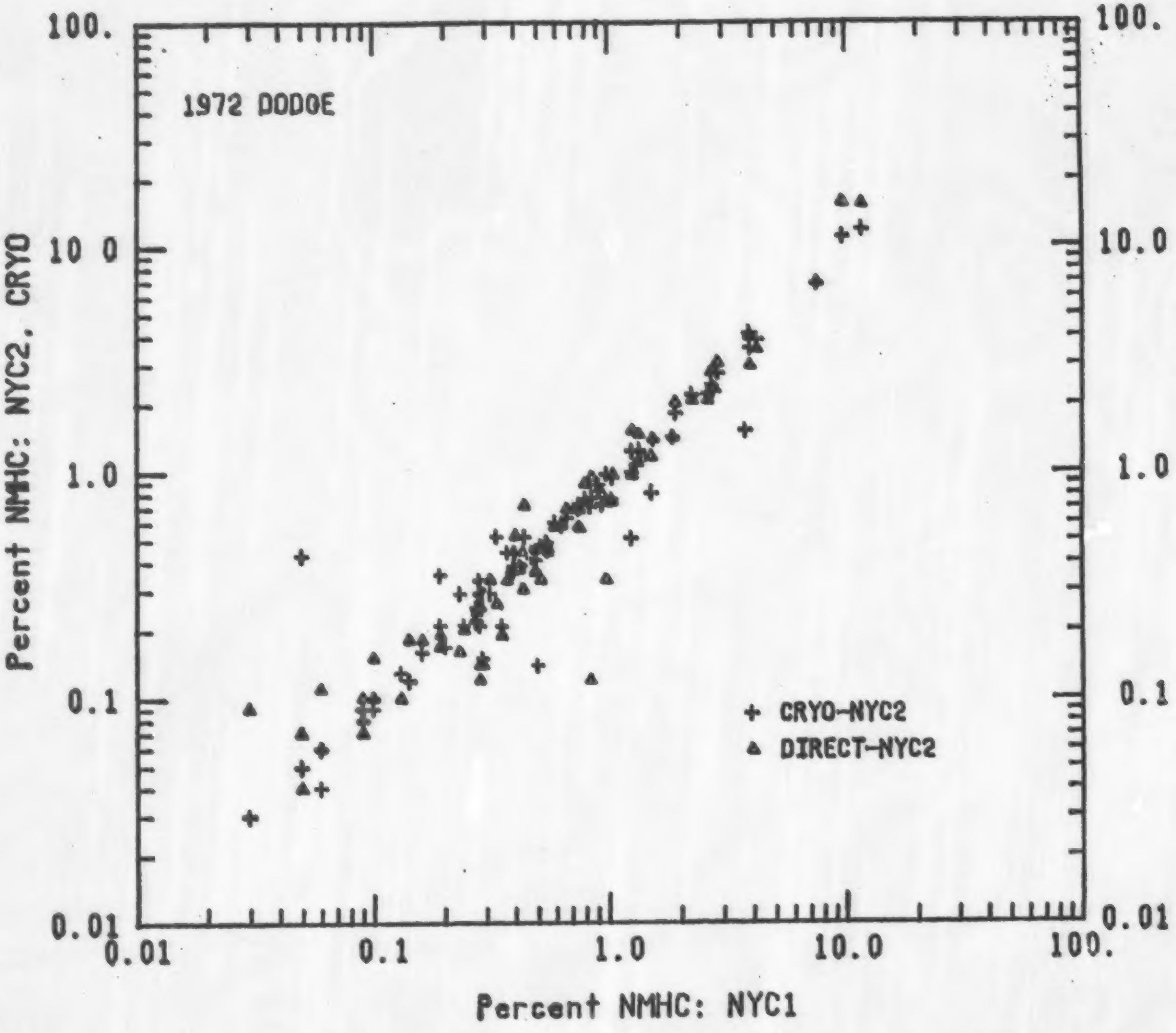


Figure 11. Species carbon percent in New York City Cycle, day 2 direct sample, and in simultaneously collected cryocondenser re-evaporated sample verses its carbon percent in New York City Cycle, day 1 direct sample.

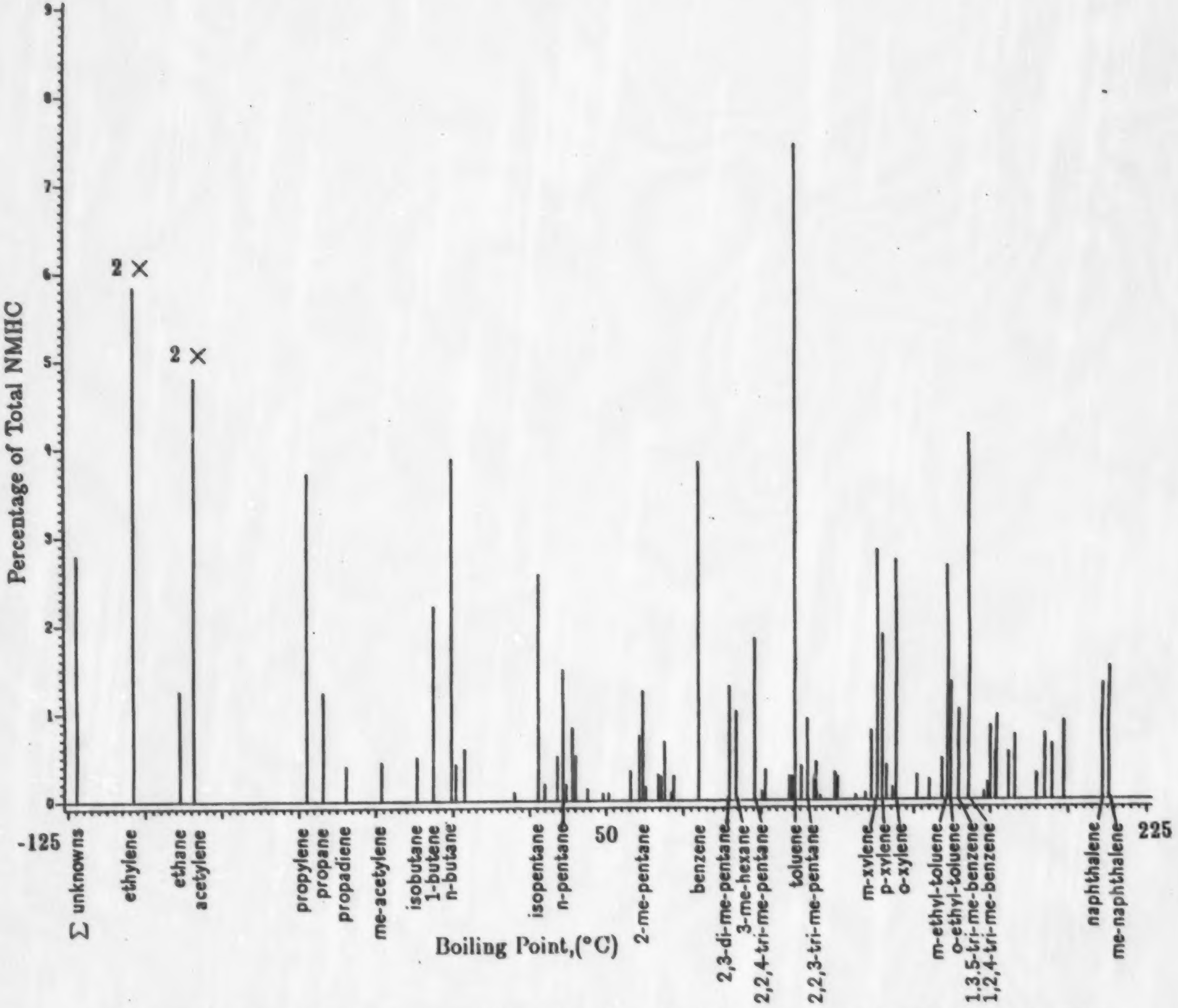


Figure 13 Hydrocarbon fractional composition as function of species boiling point for direct sample of New York City Cycle dynamometer test. Compounds above one percent are labeled.

Table 13.

Highest Concentration Hydrocarbons in Auto Exhaust Samples from Dynamometer Tests of 1972 Dodge

(percent of total nonmethane hydrocarbon)

Compound	NYC1	CRYO1	NYC2	CRYO2	IDLE	CRYO3
ethylene	11.7	9.8	11.9	14.5	15.9	18.7
acetylene	9.6	7.3	11.0	12.0	10.3	9.1
Subtotal	21.3	17.1	22.9	26.5	26.2	27.8
toluene	7.4	6.4	6.8	6.5	5.3	5.3
m,p-xylene	4.7	4.9	4.6	5.0	2.6	2.6
benzene	3.8	3.9	4.1	4.0	6.7	5.6
1,2,4-tri-me-benzene	4.1	3.9	3.8	3.5	3.7	4.2
propylene	3.7	4.0	1.5	*	3.8	4.3
m-ethyl-toluene	2.7	3.2	2.4	2.7	1.9	2.0
n-butane	3.9	3.2	3.5	3.0	1.9	1.7
o-xylene	2.7	2.7	2.3	2.3	1.0	1.9
iso-pentane	2.6	2.2	2.2	2.1	0.9	0.5
1-butene	2.2	2.2	2.2	2.1	1.7	1.8
2,2,4-tri-me-pentane	1.8	1.8	1.4	1.4	2.4	3.3
ethane	1.3	1.3	1.2	1.5	1.7	2.5
n-pentane	1.5	1.3	0.8	1.1	1.2	0.5
me-naphthalene	1.5	1.5	1.4	1.4	1.3	1.0
naphthalene	1.3	1.4	1.3	1.5	1.1	0.8
o-ethyl-toluene	1.3	4.8	1.2	1.1	*	0.6
propane	1.2	1.4	0.5	*	1.2	1.4
2-me-pentane	1.2	1.0	1.0	1.0	0.8	0.4
1,3,5-tri-me-bezene	1.0	1.7	1.0	1.0	*	0.5
Subtotal	49.9	53.1	43.2	41.6	38.4	40.5
Total	71.2	70.2	66.1	68.1	64.6	68.3

Direct sample analysis percentages are based on summed total of measured species; cryocondenser sample analysis, percentages based on assumed total concentrations of: 130.3 ppmC, 162.8 ppmC, and 36.2 ppmC due to water interference with ethylene and acetylene measurements. Captions have same meaning as those in Table 2. Columns with " * " had no values reported.

Table 14.
Hydrocarbon Class Composition During Dynamometer Tests of 1972 Dodge
(percent of total nonmethane hydrocarbon)

Composition :

Class	NYC1	CRYO1	NYC2	CRYO2	IDLE	CRYO3
Paraffins	24	23	21	10	13	15
Olefins	24	24	21	21	28	33
Aromatics	37	40	36	35	31	34
Acetylene	10	7	12	12	10	9
Unknowns	3	5	10	12	17	9
Total Number Of Compounds In Analysis :						
	96	96	96	93	80	81

FTP1,FTP2 — Federal Test Procedure day 1 and day 2, first figure for bag 1 only, second figure is for weighted total of three bags; NYC1,NYC2 — New York City Cycle day 1 and day 2; CRYO1,CRYO2 — NYC1,NYC2 test cryocondenser sample; IDLE — 2800 RPM idle; CRYO3 — IDLE test cryocondenser sample; GAS — Union 76 NoLead Regular gasoline analysis.

Composition of Gasolines Used

Four gasolines were used in this project:

- Union 76 Non Leaded Regular
  - the "standard gasoline" used in the MSERB VOC study
  - used in Dodge Charger in the 1982 dynamometer tests
  - used in early 1982 chamber runs
- Amoco Premium
  - used in Plymouth Volare in 1982 dynamometer tests
  - used in the two gasoline comparison in 1983 chamber tests
- Phillips 66 Non Leaded Regular
  - the "standard UNC test gasoline" used in late 1982 and all of 1983 chamber runs used in 1983 and 1984 dynamometer tests
- Texaco Non Leaded Gasoline
  - a large stock at the UNC General Storeroom was used on a few occasions.

MSERB supplied analyses of the first three gasolines. We applied the corrections described above and entered the data into our ANALYZHC program. The normalized carbon fraction data for the gasolines are listed in Appendix C. Figure 13 shows the class fraction composition of the three gasolines. All analyses had about 10% unknowns. The two regular gasolines had about an equal amount of carbon in the paraffin and aromatic fraction, while the premium gasoline had significantly more aromatics. All gasolines were **unleaded**.

In Figure 14 the individual HC species in the two regular gasolines are plotted against each other. The species that deviate are labelled. The Phillips 66 gasoline had more benzene than the Union 76, while the Union 76 had more toluene. The Reid Vapor Pressure of the Phillips 66 gasoline was 10.9 lbs/in^2 and was 12.2 lbs/in^2 for the Union 76 gasoline.[16]

Figure 15 compares the composition of the Amoco Premium gasoline with the Phillips 66 Regular gasoline. The Premium blend is dominated by the high toluene fraction. The rest of the blend is not much different from the regular blend.

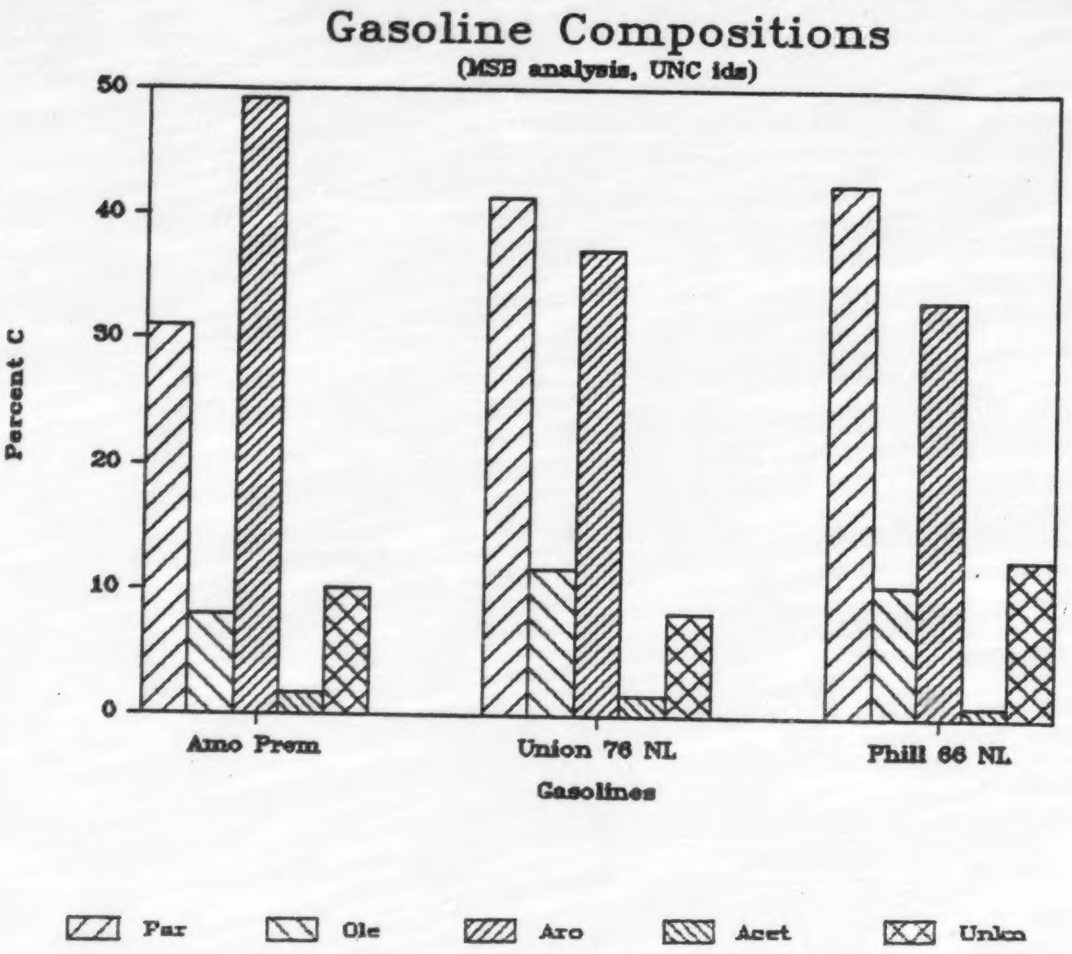


Figure 13 . Class Composition of three gasolines used in dynamometer and chamber runs.

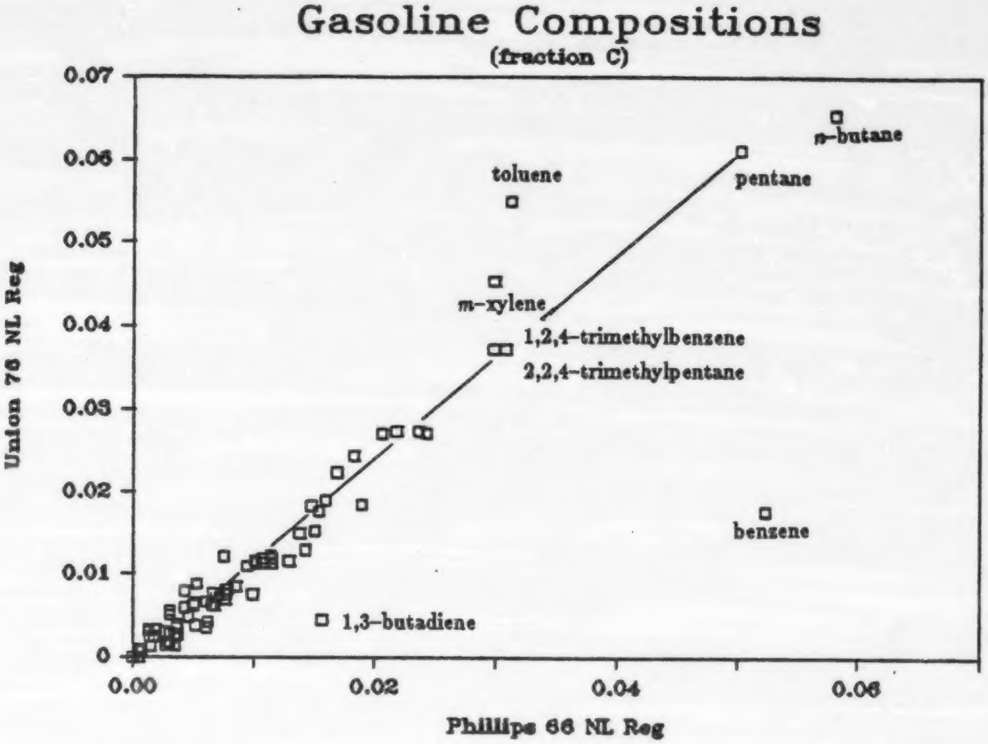


Figure 14. Union 76 Non-Lead Regular gasoline composition (fraction of C) compared with Phillips 66 Non-Leaded Regular gasoline (fraction of C).

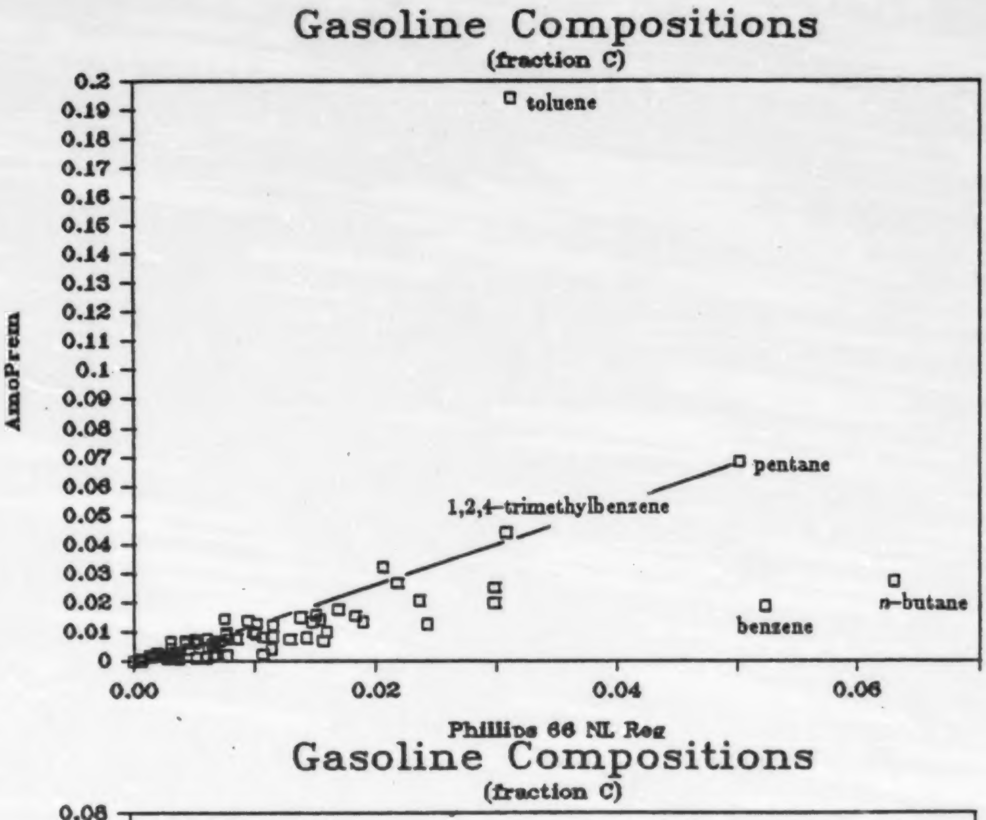


Figure 15. Amoco Premium Non-Leaded gasoline composition (fraction of C) compared with Phillips 66 Non-Leaded Regular gasoline (fraction of C). **Top:** toluene is the major species in the Premium gasoline. **Bottom:** expanded axis.

Composition of Exhaust Based On MSERB Data

The raw MSERB data from the bag analysis of the 1982 and 1983 tests of the Dodge Charger and Plymouth Volare were entered into UNC's HC analysis system. The species identifications changes described above were applied to all the dynamometer HC species data. Finally, the MSERB data were converted to percent of total NMHC in the sample; these are shown in Table 15 and Table 16 for 1982 tests; these results also appear graphically later.

It is important to note that in the hot idle sample, only 80 compounds—including unknowns—were reported and of these 17% were identified as unknown. This was because the total NMHC in the idle bag was only about 40 ppmC compared to the 160 ppmC in the other bags. Thus, the class fractions in this analysis are highly suspect. Note, however, that the average percent carbon in each class of all the analyses except the hot idle were very consistent. If the unknown material in the hot idle sample is divided so as to produce a similar average carbon number in the idle classes, then the composition would be that given in the IDLE* column.

Composition of Exhaust Based on UNC Data

In March of 1984, both cars were taken to MSERB to be run on the dynamometer in two modes while cryocondenser samples were taken. The Dodge Charger was run in a full FTP cycle (including the cold start) and in a "hot" high idle and cryocondenser samples were taken in each test. The Charger was fueled with the UNC gasoline (Phillips 66 regular non-leaded). The Plymouth Volare was run in a full FTP cycle (including cold start) but the high idle test was not done until the next morning at the site with the car cold.

The cryocondenser contents were evaporated into four bags and were diluted to about 300 ppmC. The bags were analyzed on all Carle GCs and on the Sigma 2 cryogenically programmed capillary GC. The simultaneous analysis on all instruments with a number of peaks appearing on each instrument allowed the data from all instruments to be placed on a single basis. Extensive calibrations and retention time determinations using standards allowed for reliable identification of the species. Appendix B lists the standards used.

Figure 16 is an example of the actual chromatogram from the Sigma 2 system. The Sigma 2 GC and integrator were able to measure the area of 102 peaks. Positive species identification, using the standards, was possible for the 46 peaks that each comprised more than 0.3% of the sample. An additional 34 species identifications were estimated by comparison of the sample chromatogram patterns with UNC's GC/MS identifications, by boiling point/retention time data, and, lastly, by comparison with MSERB analysis. The remaining 42 peaks (about 3% of the total area) were summed into an unknown fraction with an estimated average carbon number of 10. The detailed data for this analysis is listed in Table 17.

Figure 17, Figure 18, Figure 19, and Figure 20 show "line chromatograms" for all four sets of analysis.

The class fractions calculated from all analyses, all years, are shown graphically in Figure 21 for all samples and for the average FTP composition from the 46-car MSERB VOC tests.

Table 18 and Table 19 give the HC class composition for the 1984 tests.

Table 15.
Hydrocarbon Class Composition During MSB 1982 Dynamometer Tests of 1979 Plymouth Volare
(percent of total nonmethane hydrocarbon)

Composition :

Class	FTP1	FTP2	NYCC1	IDLE
Paraffins	22	20	21	20
Olefins	17	18	19	21
Aromatics	51	52	50	40
Acetylene	4	5	3	5
Unknowns	5	5	6	12
Total Number Of Compounds in Analysis :				
	84	84	84	84

FTP1,FTP2 — Federal Test Procedure day 1 and day 2; NYC1 — New York City Cycle day 1 ; IDLE — 2800 RPM hot idle; GAS — Amoco Premium gasoline analysis.

Table 16.
Hydrocarbon Class Composition During MSB 1982 Dynamometer Tests of 1972 Dodge Charger
(percent of total nonmethane hydrocarbon)

Composition :

Class	FTPf1	FTP	FTP	FTPt2	NYCC1	NYCC2	IDLE	IDLE*
Paraffins	27	25	24	25	24	21	13	18
Olefins	24	19	26	30	24	21	28	29
Aromatics	34	84	33	28	37	36	31	35
Acetylene	11	13	10	10	10	12	10	10
Unknowns	6	7	6	5	3	10	17	7
Total Number Of Compounds In Analysis :								
	96	96	96	96	96	96	80	

FTPf1,FTPf2 — Federal Test Procedure day 1 and day 2, first bag 1 only; FTPt1,FTPt2 — Federal Test Procedure day 1 and day 2, total test; NYC1,NYC2 — New York City Cycle day 1 and day 2; IDLE — 2800 RPM idle; IDLE* — Idle with unkn distributed; GAS — Union 76 NoLead Regular gasoline analysis.

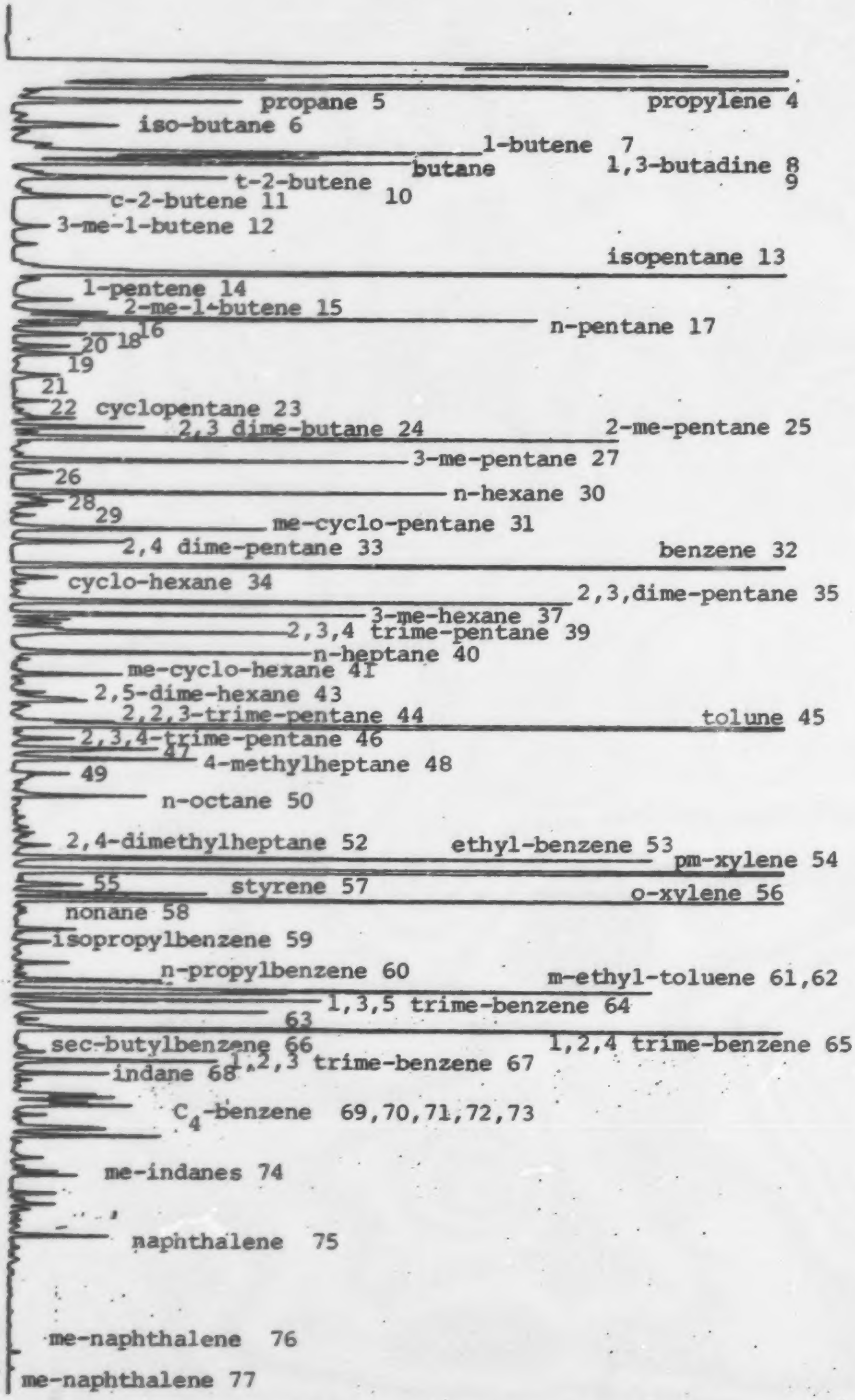


Figure 16. Sigma 2 analysis of cryocondenser sample from Dodge Charger FTP test, 1984.

Table 17. 1984 GC Chromatogram Peak Identification

Peak Id	Compound Name	Boil Pt	% NMHC	C#
0	UNKNOWNS	-122.5	2.40	1.0
1	ETHYLENE	-103.7	10.66	2.0
2	ETHANE	-88.6	0.80	2.0
3	ACETYLENE	-84.0	13.41	2.0
4	PROPYLENE	-47.4	4.28	3.0
5	PROPANE	-42.1	1.16	3.0
6	ISOBUTANE	-11.7	0.58	4.0
7	1-BUTENE	-6.3	0.99	4.0
8	1,3-BUTADIENE	-4.4	1.05	4.0
9	N-BUTANE	-0.5	3.37	4.0
10	TRANS-2-BUTENE	0.9	0.38	4.0
11	CIS-2-BUTENE	3.7	0.34	4.0
12	3-METHYL-1-BUTENE	20.0	0.21	5.0
13	ISOPENTANE	27.8	3.44	5.0
14	1-PENTENE	30.0	0.19	5.0
15	2-METHYL-1-BUTENE	31.2	0.30	5.0
16	2-METHYL-1,3-BUTADIENE	34.0	0.29	5.0
17	N-PENTANE	36.0	1.63	5.0
18	TRANS-2-PENTENE	36.3	0.16	5.0
19	CIS-2-PENTENE	36.9	0.21	5.0
20	3-METHYL-2-BUTENE	38.7	0.20	5.0
21	2-METHYL-2-BUTENE	39.0	0.21	5.0
22	CYCLOPENTENE	44.0	0.10	5.0
23	CYCLOPENTANE	49.0	0.13	5.0
24	2,2-DIMETHYLBUTANE	50.0	0.41	6.0
25	2-METHYLPENTANE	62.0	1.80	6.0
26	1-HEXENE	63.0	0.17	6.0
27	3-METHYLPENTANE	63.6	1.17	6.0
28	2-HEXENE	68.0	0.17	6.0
29	CIS-2-HEXENE	68.8	0.11	6.0
30	N-HEXANE	69.0	1.17	6.0
31	METHYLCYCLOPENTANE	71.8	0.76	6.0
32	BENZENE	80.0	5.46	6.0
33	2,4-DIMETHYLPENTANE	80.5	0.33	7.0
34	CYCLOHEXANE	81.0	0.16	6.0
35	2,3-DIMETHYLPENTANE	89.8	1.63	7.0
36	2-METHYLHEXANE	90.0	0.23	7.0
37	3-METHYLHEXANE	92.0	1.04	7.0
39	2,2,4-TRIMETHYLPENTANE	98.0	1.12	8.0
40	N-HEPTANE	98.4	0.91	7.0
41	METHYLCYCLOHEXANE	100.9	0.35	7.0
42	2,5-DIMETHYLHEXANE	109.0	0.27	8.0
43	2,4-DIMETHYLHEXANE	110.0	0.48	8.0
44	2,2,3-TRIMETHYLPENTANE	110.0	0.27	8.0
45	TOLUENE	111.0	10.90	7.0
46	2,3,4-TRIMETHYLPENTANE	113.4	0.25	8.0
47	2,3,3-TRIMETHYLPENTANE	115.0	0.63	8.0
48	4-METHYLHEPTANE	117.7	0.63	8.0
49	2,2,5-TRIMETHYLHEXANE	124.0	0.32	9.0
50	N-OCTANE	125.0	0.45	8.0
51	2,3,5-TRIMETHYLHEXANE	131.3	0.15	9.0
52	2,4-DIMETHYLHEPTANE	133.5	0.18	9.0
53	ETHYLBENZENE	136.2	1.66	8.0
54	M-XYLENE	139.1	5.69	8.0
55	3-METHYLOCTANE	143.0	0.32	9.0
56	O-XYLENE	144.0	2.07	9.0
57	STYRENE	145.0	0.56	8.0
58	NONANE	150.8	0.29	9.0
59	ISOPROPYLBENZENE	152.4	0.17	9.0
60	N-PROPYLBENZENE	159.0	0.47	9.0
61	M-ETHYLTOLUENE	161.0	1.72	10.0
62	P-ETHYLTOLUENE	162.0	0.62	10.0
63	O-ETHYLTOLUENE	162.0	0.83	10.0
64	1,3,5-TRIMETHYLBENZENE	164.7	0.81	9.0
65	1,2,4-TRIMETHYLBENZENE	169.3	2.65	9.0
66	SEC-BUTYLBENZENE	173.0	0.20	10.0
67	1,2,3-TRIMETHYLBENZENE	176.1	0.62	9.0
68	INDANE	176.5	0.27	9.0
69	1,3-DIETHYLBENZENE	181.0	0.57	10.0
70	BUTYLBENZENE	183.0	0.50	10.0
71	1,2-DIETHYLBENZENE	183.4	0.56	10.0
72	1,4-DIETHYLBENZENE	183.8	0.42	10.0
73	TETRAMETHYLBENZENE	198.0	0.33	10.0
74	METHYL-INDANE	0.0	0.14	10.0
75	NAPHTHALENE	211.0	0.26	10.0
76	1-METHYLNAPHTHALENE	212.0	0.03	11.0
77	2-METHYLNAPHTHALENE	213.0	0.01	11.0

a) GC Analysis report for Dodge Charger. FTP, 1984 by UNC
b) Peak Id - numbers identifying compounds on all 1984 GC chromatograms
c) C# - Carbon Number

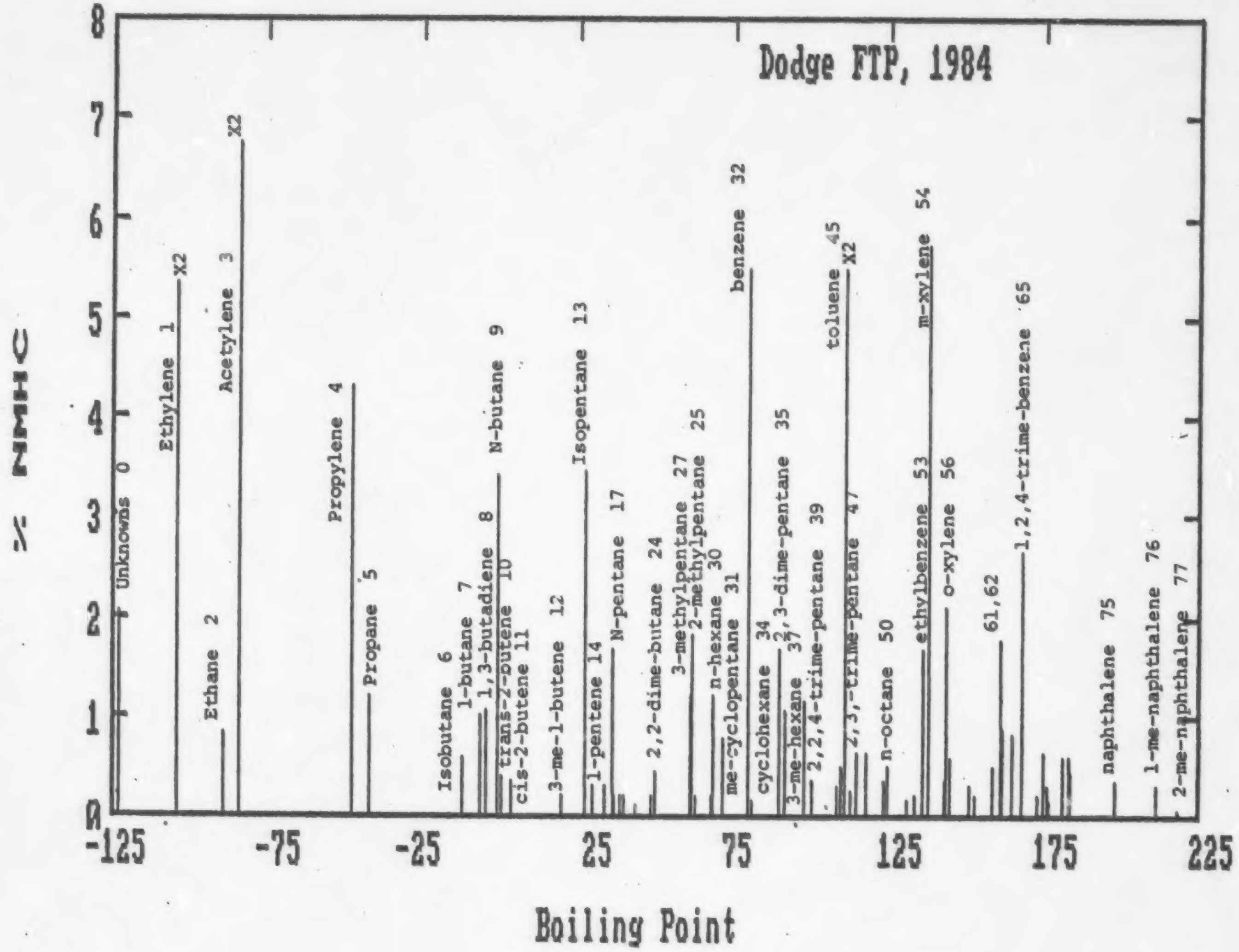


Figure 17 . Line chromatograms constructed from four UNC gas chromatographic instruments used to analyze cryocondenser samples.

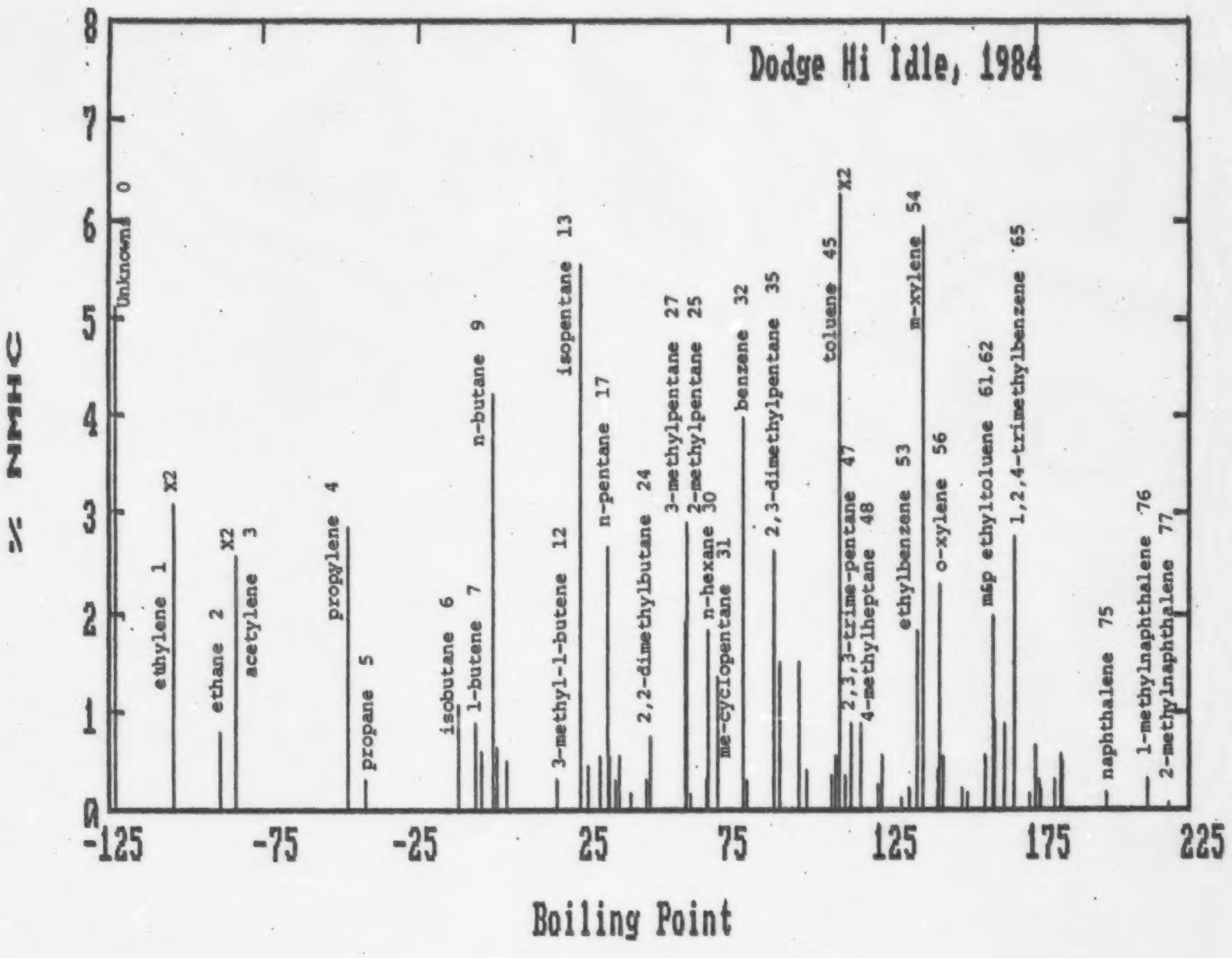


Figure 18. Line chromatograms constructed from four UNC gas chromatographic instruments used to analyze cryocondenser samples.

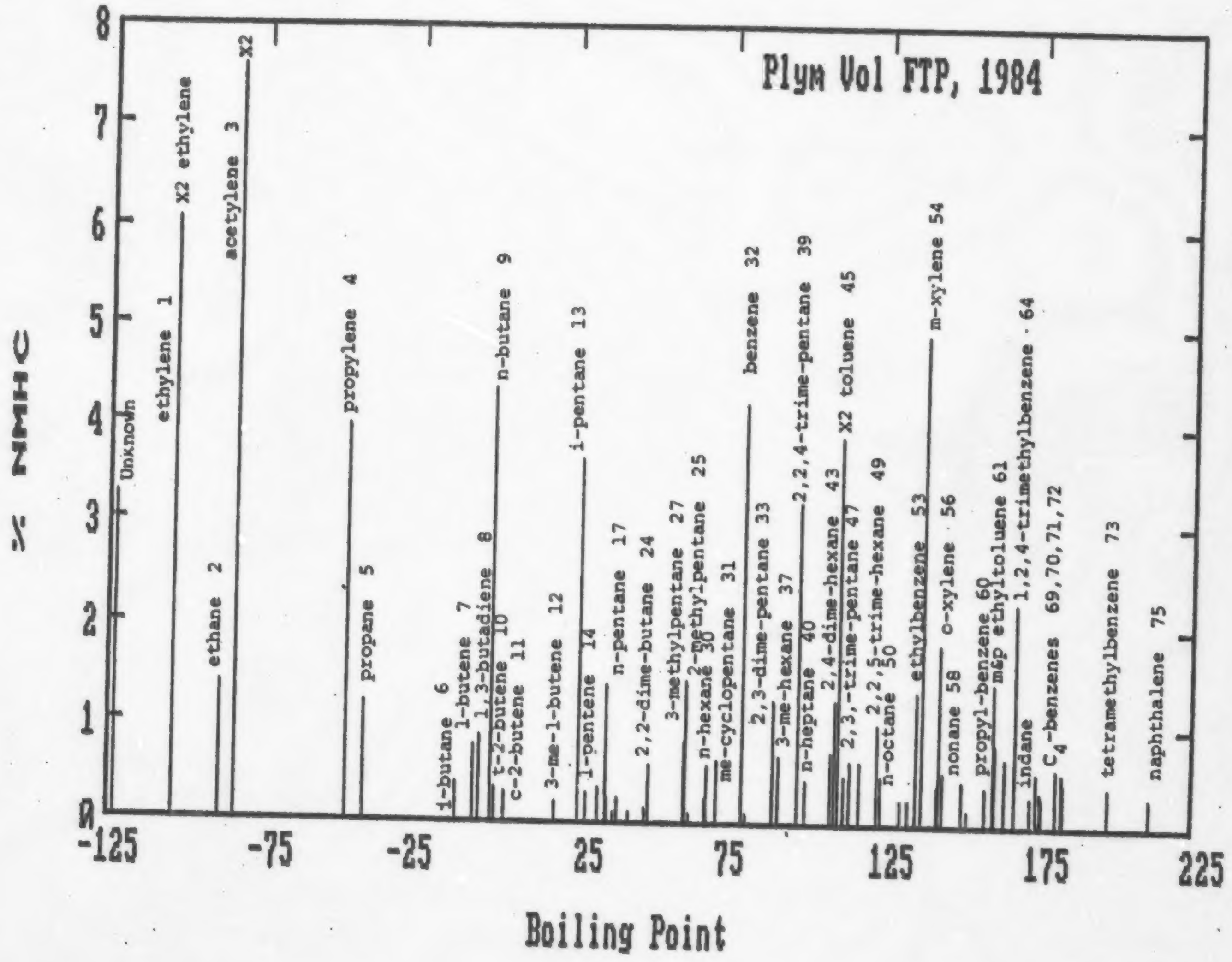


Figure 19 . Line chromatograms constructed from four UNC gas chromatographic instruments used to analyze cryocondenser samples.

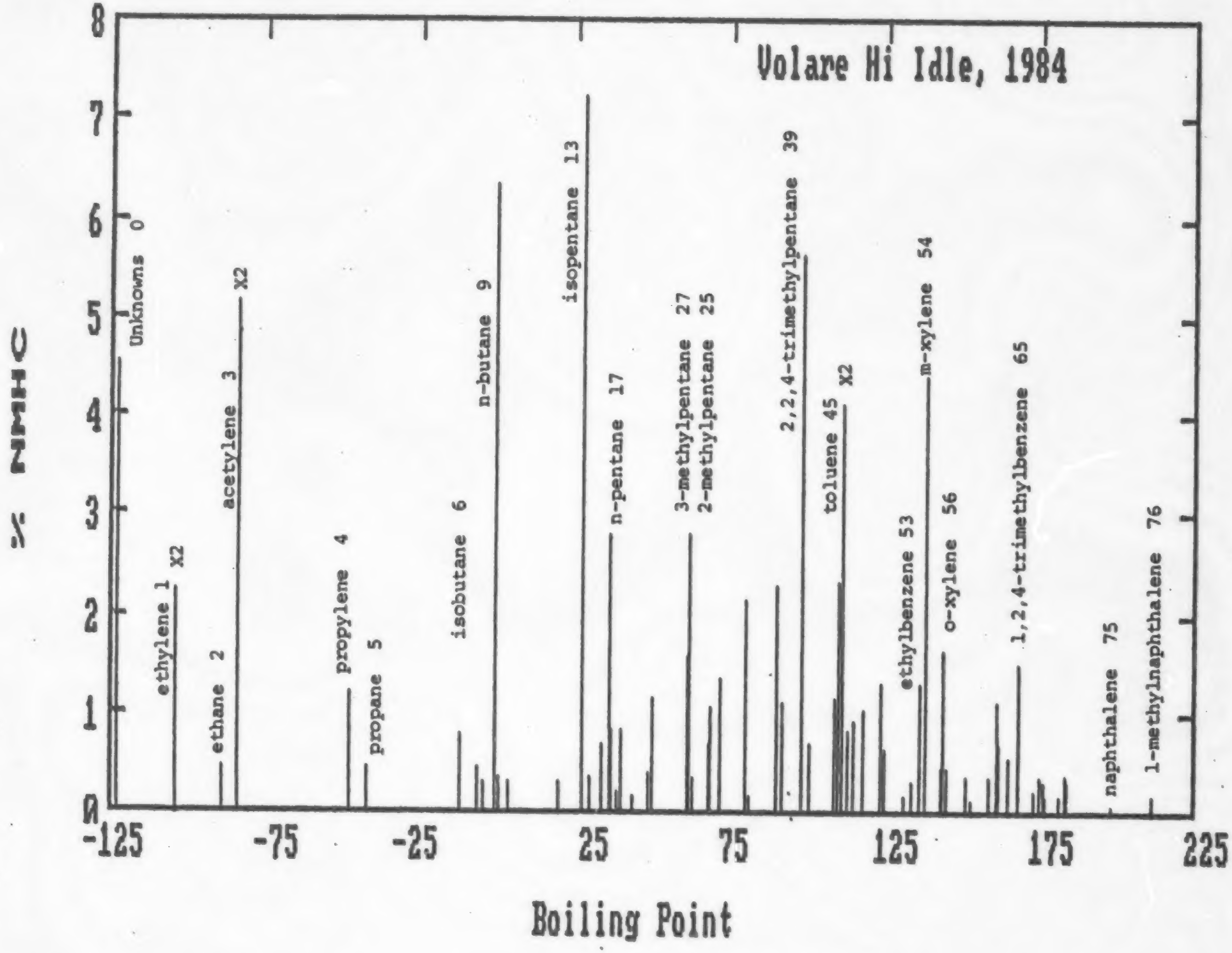


Figure 20 . Line chromatograms constructed from four UNC gas chromatographic instruments used to analyze cryocondenser samples.

Table 18.
Hydrocarbon Class Composition During UNC 1984 Dynamometer Tests of 1979 Plymouth Volare
(percent of total nonmethane hydrocarbon)

Composition †

Class	FTPt	C no.	IDLE	C no.	GAS
Paraffins	30	5.3	48	5.8	39
Olefins	20	2.4	11	3.0	10
Aromatics	30	7.9	24	7.8	48
Acetylene	15	2.0	11	2.1	0
Unknowns	4		5		2

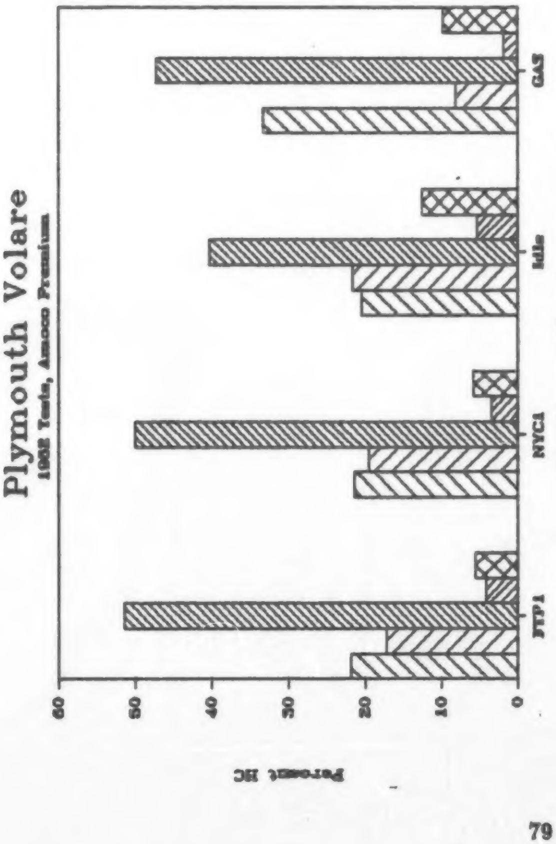
FTPt — Federal Test Procedure, cycle average; IDLE — 2800 RPM hot idle; GAS — Phillips 66 NoLead Regular gasoline analysis.

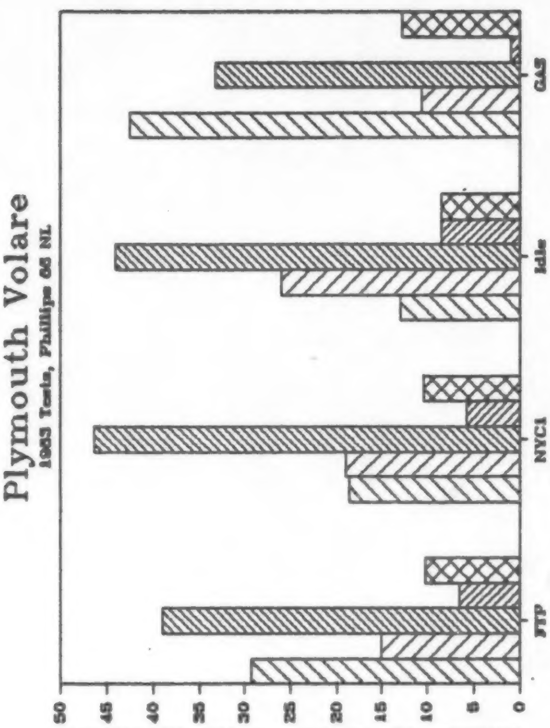
Table 19.
Hydrocarbon Class Composition During UNC 1984 Dynamometer Tests of 1972 Dodge Charger
(percent of total nonmethane hydrocarbon)

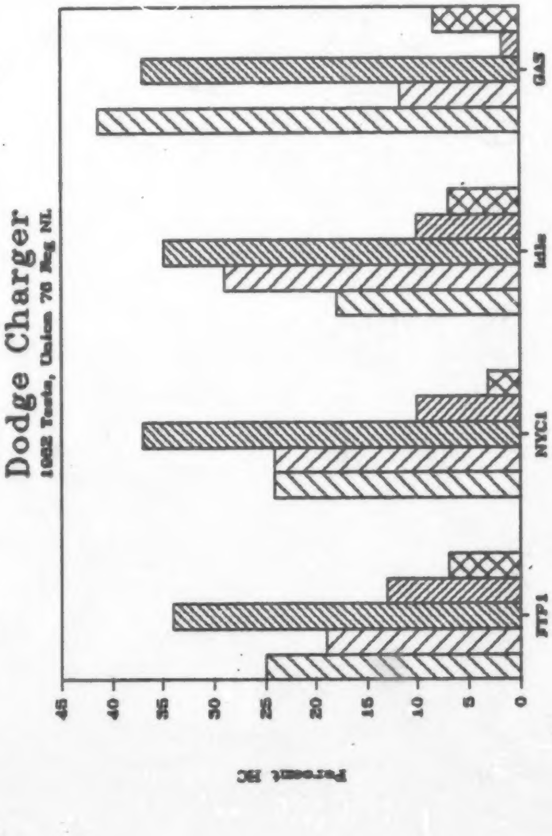
Composition :

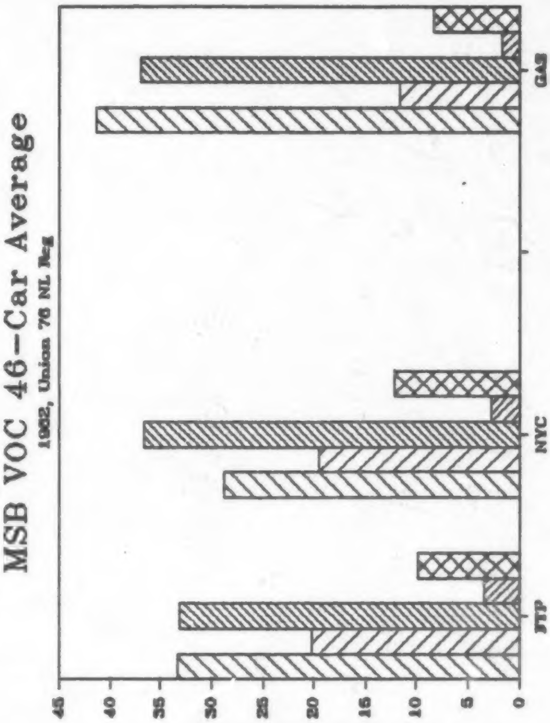
Class	FTPt	C no.	IDLE	C no.	GAS
Paraffins	27	5.3	36	5.5	48
Olefins	20	2.5	15	2.8	8
Aromatics	37	7.8	38	7.8	35
Acetylene	14	2.0	5	2.1	0
Unknowns	2		6		8

FTPt — Federal Test Procedure, cycle average; IDLE — 2800 RPM hot idle; GAS — Union 76 NoLead Regular gasoline analysis.


Plymouth Volare
1982 Tests, Amoco Premium
Percent HC
0
10
20
30
40
50
60
FTP1
NYC1
Idle
GAS


Plymouth Volare
1983 Tests, Phillips 66 NL
0
5
10
15
20
25
30
35
40
45
50
FTP
NYC1
Idle
GAS


Dodge Charger
1982 Tests, Union 76 Reg NL
Percent HC
0
5
10
15
20
25
30
35
40
45
FTP1
NYC1
Idle
GAS


MSB VOC 46-Car Average
1982, Union 76 NL Reg
0
5
10
15
20
25
30
35
40
45
FTP
NYC
GAS

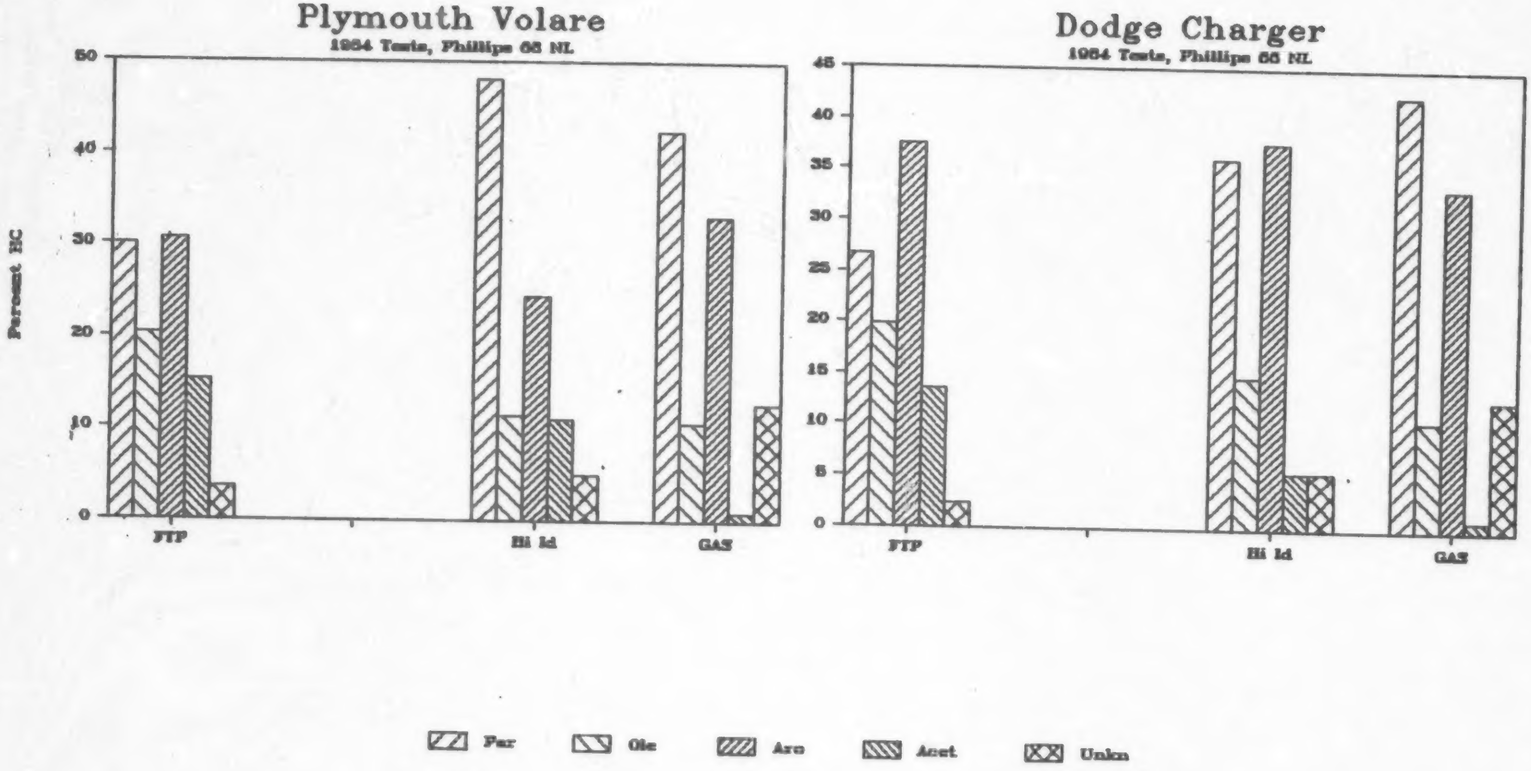


Figure 21 . Exhaust hydrocarbon class composition (percent C) for MSB dynamometer test of 1979 Plymouth Volare and 1972 Dodge Charger. The 1982 and 1983 species measurements were performed by MSB and the raw data were supplied to UNC. The 1984 analysis was performed by UNC on cryocondenser–collected samples transported from MSB. Symbols and labels are: FTP, Federal Test Procedure for dynamometer; NYC, New York City cycle dynamometer test; IDLE, hot 2200 rpm idle test; GAS, composition of gasoline used for test.

Comparison of UNC and MSERB HC Analysis

In the 1984 dynamometer tests, the cryocondenser sample taken at MSERB was transported to the UNC site and vented into a bag; MSERB took a sample during the dynamometer test for a duplicate analysis. The MSERB data were treated as described above in the cryocondenser discussion (*i.e.* the species identifications were changed and splitting factors were applied by UNC). The HC class fraction data calculated from these analyses are compared in Figure 22 and are listed in Appendix C. UNC reports ≈5% more paraffins, 3% more acetylene, and less aromatics than MSERB in this comparison.

In a second comparison test, one of UNC's standard high concentration HC calibration tanks (dry sample in nitrogen) was used as a sample and sent to MSERB for analysis. The tank contained 13-components, from acetylene to ethyl-benzene, all at or near 20 ppmC.

In this analysis, the problems with the poor performance of the first column in the MSERB analysis system was revealed: 12 ppmC of *iso*-butane was identified as 9.97 ppmC of propylene, a significant mis-identification.

The compounds acetylene, 1-pentene, benzene, cyclohexane, and m-xylene were correctly identified at the correct concentrations.

The remaining compounds were reported with approximately the correct concentrations, but as un-resolvable peaks:

2-methyl- pentane	as	2-methyl-pentane or 2,3-dimethyl-1-butene
n-hexane	as	n-hexane or cis-3-hexene
2,3-dimethyl-pentane	as	cyclohexene or 2,3-dimethyl- pentane or 2-methyl-hexane
toluene	as	toluene or 2,3-dimethylhexane
ethyl-benzene	as	ethyl-benzene or 2,3-dimethyl-hexane
o-xylene	as	o-xylene or unk C_9 paraffin

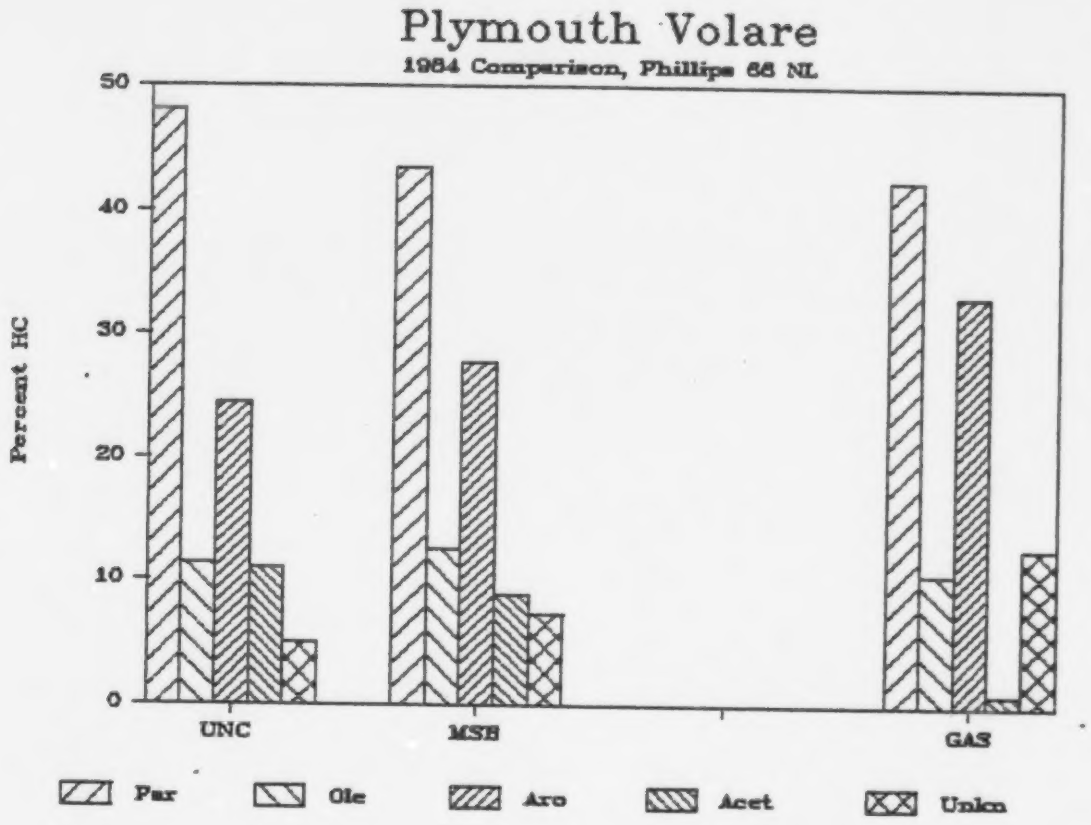


Figure 22. Comparison of class composition as determined by UNC analysis and MSERB analysis of same exhaust sample. MSERB performed the gas analysis.

Average Carbon Number in Each Class

As an aid in understanding the composition of the automobile exhaust, the average carbon number in each class was computed. These values are listed in Appendix C and are plotted in Figure 23. It was estimated that the average carbon number for paraffins was 5.15; for olefins was 2.55; and for aromatics was 7.85. These values were used in the "spreadsheet" for the initial conditions for each run to estimate the HC not detected by the site GC instruments.

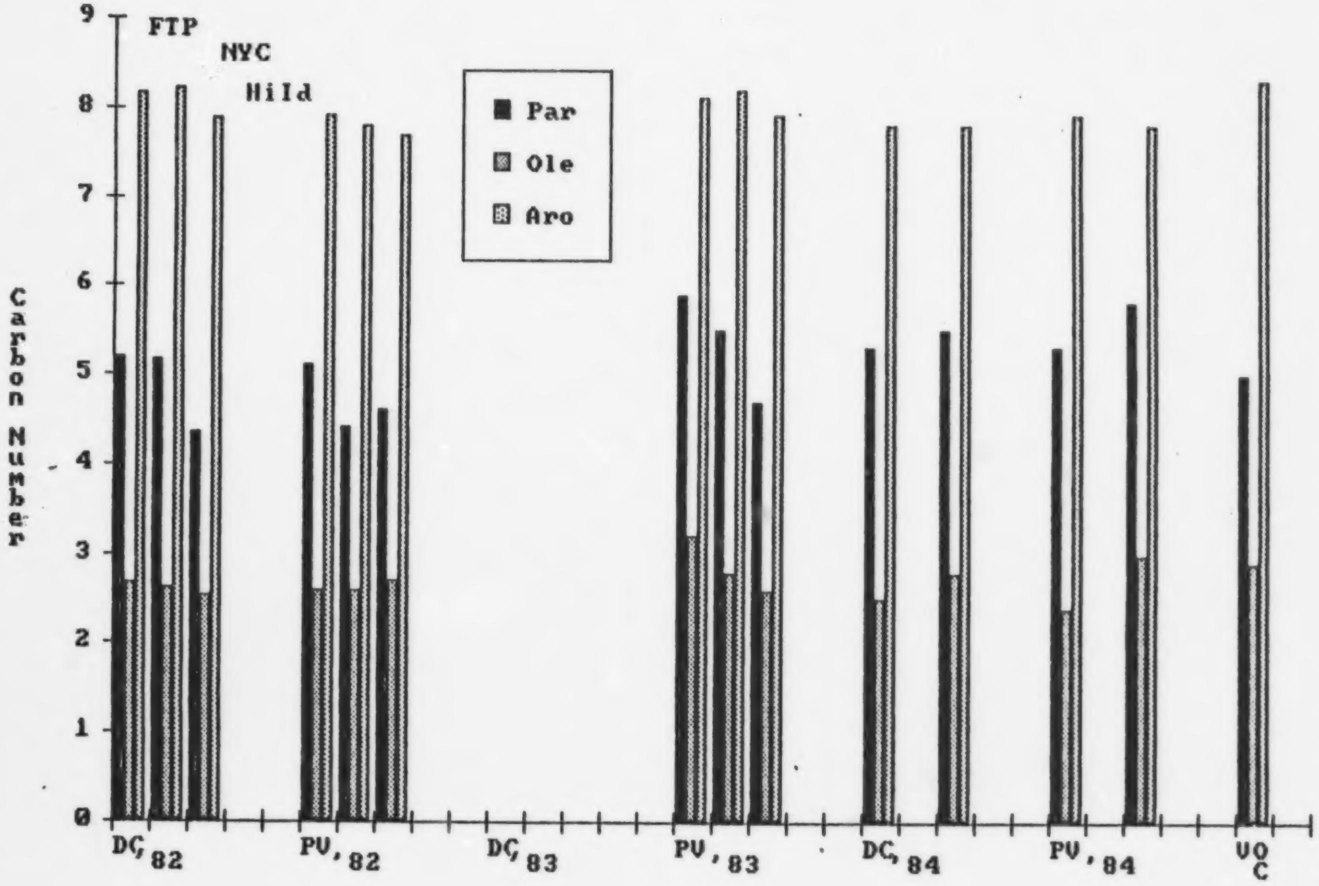


Figure 28. Average carbon number in the paraffin, olefin, and aromatic classes in each detailed analysis conducted in dynamometer tests and in the 46-car MSB VOC study. For each car-year analysis the order of tests are FTP, NYC, and high idle. The 1984 tests have no NYC analysis.

Hydrocarbon Measurements During Runs

As shown in Figure 5 (Chapter 2), about 22 compounds are present in exhaust at concentrations greater than 1% of the total NMHC. At total NMHC concentrations between 0.3 and 3.0 ppmC, even measuring these 20 or so compounds is a difficult task.

Original 1982 plans called for existing site instruments to be used to monitor the total NMHC and the 5 to 10 highest species and to depend upon MSERB's detail analysis of exhaust composition in combination with the few site measured species for the detailed model input.

As experimental data were obtained both from the dynamometer tests and the chamber experiments, we realized that the original plan for HC data was not satisfactory. New instruments were designed, the parts were purchased, the systems were constructed and placed in use in experiments as soon as was possible. In addition, calibration techniques were improved and new calibration sources were obtained. Thus the individual HC species data in the beginning of 1982 were meager; the data near the end of 1983, based upon additional instruments, were ample, often accounting for 80–90% of the NMHC.

Characteristics of Site HC Instruments

Total Hydrocarbon Instruments

A Beckman 6800 was used to measure THC, CH_4, and CO; THC was measured on one column and CH_4 and CO were measured on another column. Both columns were connected to a single detector. The major difficulty with this instrument was that CH_4 had a different response factor on the THC analysis than did higher HCs. That is, equal concentrations of CH_4 and ethane gave different amounts of signal in the detector. Thus the THC signal was composed of at least two parts: the first caused by the CH_4 in the sample and the second caused by the NMHC in the sample. Although under some circumstances aromatic species may have produced a lower signal than the same amount of alkane carbon, we believe that, in general, all NMHC compounds responded approximately the same in the THC measurement. Even if aromatic compounds did respond 20% lower, the total effect on the NMHC would only be about 7%. CH_4 appeared by itself in the second column and, therefore, could be directly calibrated. To correctly calculate NMHC from the THC signal, however, required that a methane-only response factor be determined for the THC signal.

In 1982, we did not routinely calibrate the THC response with only CH_4, and therefore alternative methods for estimating the CH_4 calibration on the THC output have been used. In 1983, both THC and CH_4 outputs were calibrated with a CH_4-standard.

The calculation of NMHC from THC and CH_4 responses is also susceptible to noise problems, in that both peaks are large, but the difference—which is the information about the NMHC—is usually small. Examples of signals are shown in Appendix B. The exact methods used to calculate NMHC for the initial concentrations of the exhaust experiments are described in Appendix D and the computer program used for the calculations is listed as documentation of the process.

One of the packed column GCs (Carle I) was equipped with a THC loop allowing an independent measurement of THC to be obtained. This was a fast measurement and it was use to balance the THC injections on the two sides of the chamber. An example of such use is given in Appendix B. Using CH_4 from the chamber background, these THC data were also used to calculate the initial NMHC injected. Comparison of these data with NMHC from the Beckman 6800 showed good agreement within about ±20%. Thus we believe that the initial NMHC data are ca. ±20% accurate. Furthermore, except when the NMHC concentrations were low (<0.5 ppmC), the calculated NMHC values are always larger than the sum of the explicit species that we can quantify on all the GCs. We believe that this difference is real and that it represents "un-specieated" HC on the GCs—that is, HC species that were lost in the baseline noise of the GC or not separated from background levels or "air" peaks and thus were not measurable.

Gas Chromatographs

Using the packed column GCs at the site, we could usually detect 0.01–0.03 ppmC of a light compound and could obtain a time profile if the compound's concentration exceed 0.1 ppmC. Typical chromatograms are shown in Appendix B. These GCs could also measure the higher concentration aromatic compounds such as benzene, toluene, and m,p-xylene.

The site packed chromatographs were designed to operate automatically and isothermally for typical smog chamber test mixtures; they were not optimized for analysis of automobile exhaust. Thus, these instruments had resolution problems given the complex nature of the exhaust. Major resolution problems were the coelution of ethylene and acetylene on the Carle II instrument and of propylene and acetylene on the Carle I instrument. (We normally do not use acetylene in test mixtures.) Furthermore, Carle I and Carle II GCs, which were the only packed GCs used in 1982, had resolution problems in the C_4 and C_5 region where exhaust is complex compared to our usual smog mixtures. Thus, the 1982 reported site species data contain no information about n-butane and the butenes because, although a large peak was detected, its composition was not known.

The PE900 capillary column GC, which was used in both 1982 and 1983, was programmed from ambient temperatures to 150°C and could separate from benzene to the C_{11}-region. Accurate measurement of benzene was a problem on this instrument, however, because of changing ambient starting temperatures. For species above C_6, detection limits were 0.005 ppmC. Thus we had better detection for aromatic compounds than for, say, propylene or ethylene. An actual morning injection chromatogram from this GC is shown in Figure 24 for the July 15, 1983 run; the total NMHC was 2.25 ppmC; the species identifications were noted by the site operator.

Calibration factors for this instrument now seem to be too high for 1982; we have no explination for why this might be so. We have used the data as they were reported, however. In 1983, the instrument sensitivity declined sharply for several runs. The problem was traced to a broken connection. The instrument did provide data for the highest concentration species during the problem period. The documentation sections for the individual data files list such problems for each run.

By 1983, we had developed a third packed GC, the Carle III, that was optimized for separation in the C_4 and C_5 region. This chromatograph also measured the higher concentration aromatics such as benzene, toluene, and m,p-xylene. We had also developed a technique to deal with the co-elution problems on the first two instruments. Near the end of the run season in 1983, we began to use the cryogenic programmed Perkin Elmer Sigma 2 capillary GC that we obtained on loan from EPA for this project. This GC could resolve more than 200 compounds between propylene and methyl naphthalene. An example chromatogram was shown in Figure 16.

Several species were measured on more than one instrument. Each instrument was frequently calibrated independently for the major species. Experience had demonstrated that electronic integrators were not capable of correctly processing

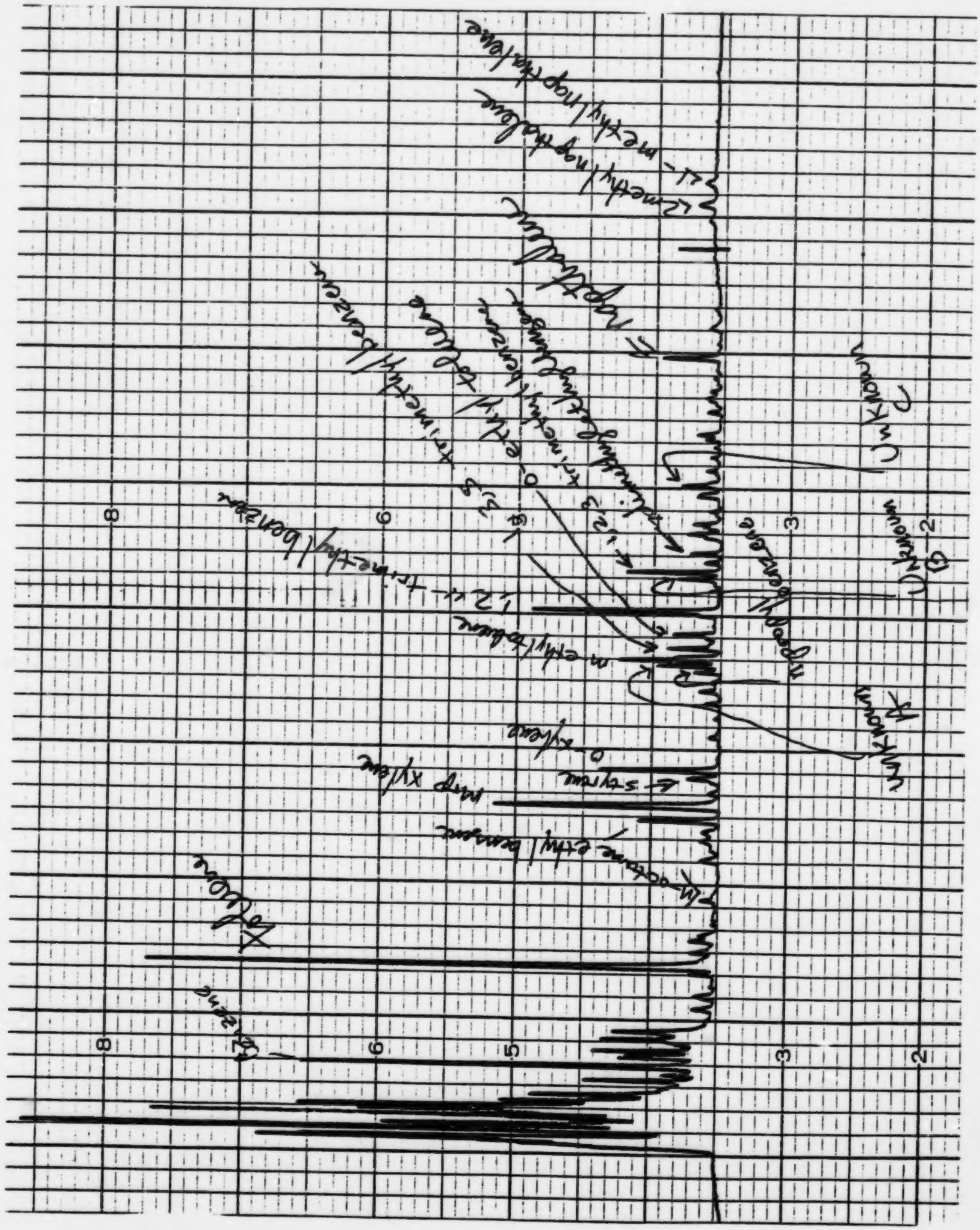


Figure 24. The PE-900 gas chromatogram of the July 15, 1983 BLUE chamber injection taken at 0541 EDT. This was a direct injection from the Dodge Charger using Phillips 66 NL regular gasoline; total NMHC: 2.25 ppmC.

data during experiments; we did use them to assist in calibrations. GC data processing was performed by a skilled data processor using an electronic digitizer connected to a computer to digitize the heights of peaks on stripcharts. The same technique was applied to calibration samples to produce calibration factors for each species. These calibration factors were applied independently to access a species concentration. Small peaks naturally have larger errors. Data from multiple instruments will be compared below. All data that are "picked" for each species on each instrument are included in the data tape file.

To summarize, HC species data for the 1982 experiments were lacking in information on C_4 to C_6 compounds; in 1983, these data were generally available. HC species data for both 1982 and 1983 experiments, except for a few runs near the end of 1983, required difference calculations to produce acetylene, ethylene, and propylene concentrations (see discussion below).

Calculation of Co-eluting Compound Concentrations

An electronic "spreadsheet" program on an IBM PC computer was used to solve for individual compound concentration and to compare concentrations of compounds measured on more than one instrument. Data from the initial sample after injection on each instrument were entered into the spreadsheet and fixed formulas in the spreadsheet compute the individual compound concentrations. These were compared among instruments and a single value was selected as the recommended value of each species initial concentration. Printouts of the "spreadsheet" for each day were included in the documentation section of each run that was added to the experimental database on magnetic tape.

Table 20 is an example of such a spreadsheet printout. It shows the calculations for the July 1, 1982 experiment in which matched direct injections from the 1972 Dodge Charger were made in each side of the chamber. The first part of the spreadsheet shown in Table 20 lists the initial concentrations reported in the data file for this day. These were the concentrations obtained by processing data from each of the chromatographs. A common spreadsheet was used for both years and so this example includes space for the `CABLE III GC` even though it was not available in 1982; the entries have been marked with `NA` meaning `Not Applicable`. The time of the sample proceeds each instrument's data. Compounds known to co-elute are entered with a + between the species names.

The next part of the spread sheet shows the calculated values using formulas in the spreadsheet cells. These were:

```
  ETHYLENE,C1 = ETHYLENE+ETHANE,C1 − ETHANE,C2
ACETYLENE,C1 = PROPYLENE+ACETYLENE,C1 − PROPYLENE,C2
ETHYLENE, C2 = ETHYLENE+ACETYLENE,C2 − ACETYLENE,C1
    ETHANE,C1 = ETHYLENE+ETHANE,C1 − ETHYLENE,C2
ACETYLENE,C2 = ETHYLENE+ACETYLENE,C2 − ETHYLENE,C1
PROPYLENE,C1 = PROPYLENE+ACETYLENE,C1 − ACETYLENE,C2
```

where `C1` means measured on Carle I GC and `C2` means measured on Carle II GC.

The next section of the spreadsheet compares the calculated values and the values reported for compounds measured on more than instrument. The line by the species name gives the absolute differences in ppmC; the second line gives the percentage differences according to the formula shown on the left of the line. Generally, species present at concentrations greater than 0.5 ppmC were reported within 5–6% of each other on different instruments. For species present at less than 0.2 ppmC, the values deviated by about 20% and for species present at less than 0.10 ppmC the deviations were about 50%. These data support the statement above that 0.01–0.03 ppmC was the detection limit on these packed column instruments.

The last part of the spreadsheet in Table 20 is a recommendation for the initial concentration of individual compounds. In some cases these recommendations were the mean value from two instruments and in some cases we selected one instrument's value over another because of the quality of the chromatogram and other factors that were essentially subjective.

Table 20. Example Calculations For Co-eluting Compounds

INITIAL CONCENTRATIONS FOR 82-83 AUTO RUNS REVISED: 07-Mar-85

RUN DATE	EXPERIMENTAL	CONCENTRATIONS.
01-Jul-82	BLUE	RED
	PPMC	PPMC
1. DATA FILE VALUES		
CARLE I GC	@0545 EDT	@0615 EDT
ETHYLENE+ETHANE	0.7015	0.6775
PROPYLENE+ACETYLENE	0.9754	0.9691
TOLUENE+OCTANE	0.3388	0.3222
BENZENE+UNKNS	NA	NA
M,P-XYLENE	0.1485	0.1397
O XYLENE	NA	NA
CARLE II GC	@0556 EDT	@0526 EDT
ETHYLENE+ACETYLENE	1.4031	1.3977
ETHANE	0.0639	0.0623
PROPYLENE	0.2482	0.2326
TOLUENE	0.3564	0.3461
CARLE III GC	@0000	@0000
TOLUENE	NA	NA
BENZENE	NA	NA
M,P-XYLENE	NA	NA
O-XYLENE	NA	NA
PE900 GC	@0630 EDT	@0710 EDT
TOLUENE	0.4120	0.4023
BENZENE	0.4756	0.4746
M,P-XYLENE	0.1960	0.1654
O-XYLENE	0.0744	0.0664

Table 20. continued

2. CALCULATED VALUES		
ETHYLENE, C1	0.6376	0.6152
ETHYLENE, C2	0.6759	0.6612
ETHANE, C1	0.0256	0.0163
ACETYLENE, C1	0.7272	0.7365
ACETYLENE, C2	0.7655	0.7825
PROPYLENE, C1	0.2099	0.1866

Table 20. continued

3. COMPARISON OF VALUES

ETHYLENE	C1-C2	-0.0383	-0.046
	(C1-C2)/C1	-6.01%	-7.48%
ETHANE	C2-C1	0.0383	0.046
	(C2-C1)/C2	59.94%	73.84%
PROPYLENE	C2-C1	0.0383	0.046
	(C2-C1)/C2	15.43%	19.78%
ACETYLENE	C1-C2	-0.0383	-0.046
	(C1-C2)/MEAN	-5.13%	-6.06%
BENZENE,	C1-PE	NA	NA
	(C1-PE)/PE	NA	NA
BENZENE,	PE-C3	NA	NA
	(PE-C3)/C3	NA	NA
TOLUENE,	C2-C1	0.0176	0.0239
	(C2-C1)/C1	5.19%	7.42%
TOLUENE,	PE-C2	0.0556	0.0562
	(PE-C2)/C2	15.60%	16.24%
TOLUENE,	PE-C1	0.0732	0.0801
	(PE-C1)/C1	21.61%	24.86%
M,P-XYLENE,	C1-PE	-0.0475	-0.0257
	(C1-PE)/PE	-24.23%	-15.54%
M,P-XYLENE,	C1-C3	NA	NA
	(C1-C3)/C3	NA	NA

Table 20. continued

4. RECOMMENED VALUES

ETHANE	(C2)	0.0639	0.0623
ETHYLENE	(MEAN)	0.6568	0.6382
ACETYLENE	(MEAN)	0.7464	0.7595
PROPYLENE	(C2)	0.2482	0.2326
BENZENE	(1)	0.4756	0.4746
TOLUENE	(2)	0.3476	0.3342
M,P-XYLENE	(3)	0.1723	0.1526
O-XYLENE	(3)	0.0744	0.0664

5. COMMENTS AND NOTES

(1) DEPENDS ON DATA QUALITY- SELECT BEST DATA FROM C3 AND PE
(2) C1 AND C3 DATA ARE BEST- C2 AND PE USUALLY GOOD.
AVERAGE BEST AVAILABLE DATA OR USE C1 ALONE.
(3) DEPENDS ON DATA QUALITY- SELECT BEST, USUALLY C3 OR PE.

Initial Concentrations of HC In Runs

One of the goals of this project was to provide guidance to modelers on the class distribution of HC as well as the concentrations of selected species. To accomplish this goal, a second spreadsheet was created for each run that was processed for the data tape.

The example spreadsheet that will be discussed is shown later in the data presentation for the August 11, 1983 experiment. In this experiment, different concentrations of exhaust were injected into the two chamber halves, but the same initial NO_x was used. In effect, there was a HC reduction of 63% between the two sides.

The spreadsheet on pages 182–184 shows the individual compounds that were measured (or in some cases detected but not quantified) from all instruments on both sides of the chamber for the initial analysis. The compounds are arranged by HC class. In listing the species measured, the following conventions have been used:

Code	Meaning	Comments
ND	not detected	no signals above baseline noise were detected
NM	not measured	no instruments capable of separating species
NA	not applicable	calculation is not applicable
T	trace	concentration near detection limit
0.00	measured zero	compound was not present

The spreadsheet also included initial NMHC concentrations from the Beckman 6800 instrument. The difference between the sum of the GC measured species and the NMHC measurement was called the `Unspeciated Carbon` on the spreadsheet. The spreadsheet also computed the percent distribution of the carbon using the NMHC as the total carbon. In the case of August 11, 1983, the measured NMHC was 0.678 ppmC on the BLUE side and 2.151 ppmC on the RED side. The sum of the GC measured carbon was 0.623 ppmC on the BLUE and 1.945 ppmC on the RED side and therefore the carbon not reported as individual species was 0.055 ppmC on the BLUE side and 0.206 ppmC on the RED side.

To estimate the HC class of this "unspeciated carbon" two other sources of information were used: the average carbon number in each class, as shown in Figure 23, and an estimate of the likely fractional distribution of carbon by class. The latter subject will be discussed in the next chapter. In the `SUMMARY` part of the spreadsheet,

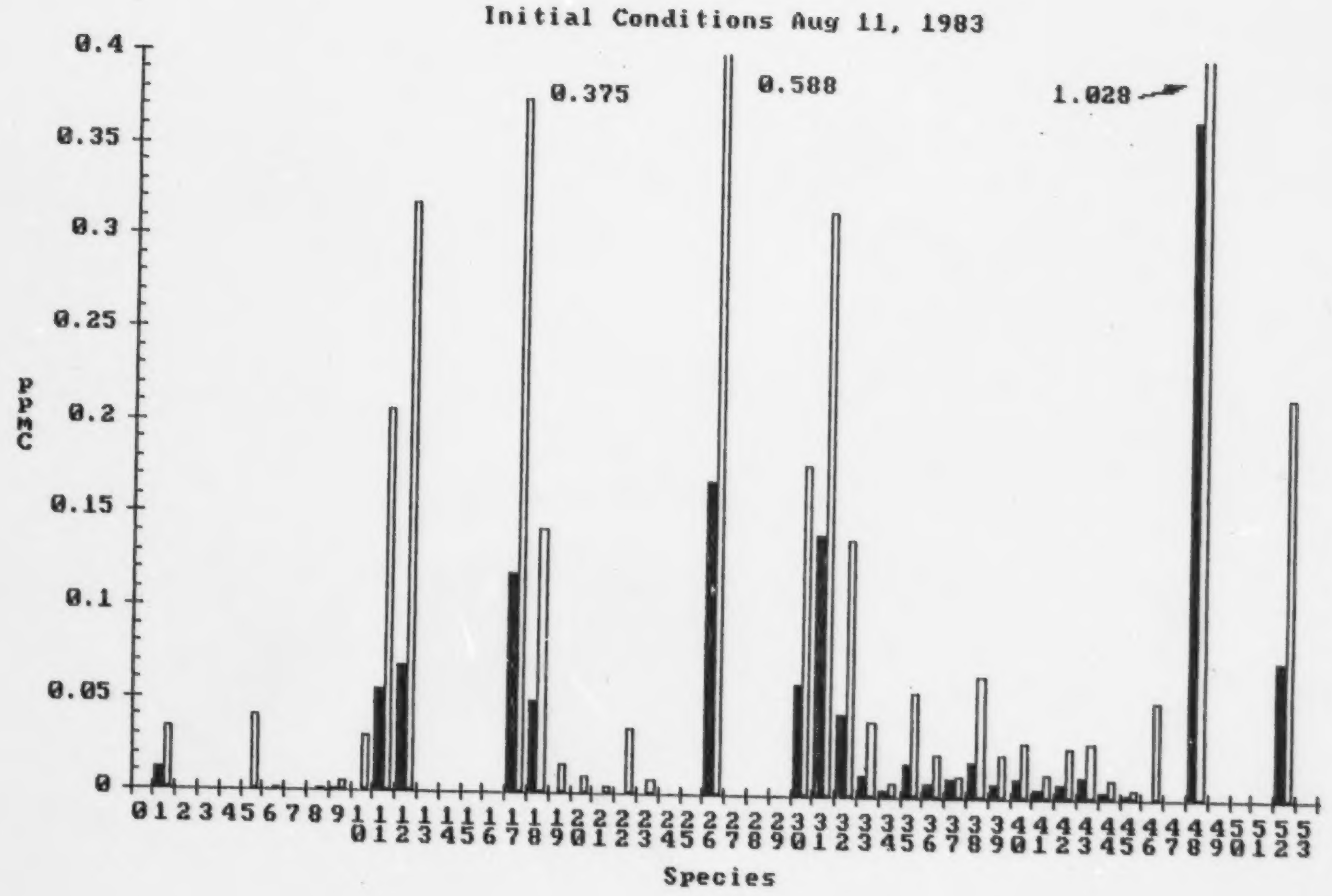


Figure 25. A comparison of side-by-side injection and analysis in an EKMA-type experiment. Species: 1-10, paraffins; 11, sum of paraffins measured; 12, sum of paraffins with estimated composition; 17-24, olefins; 26, sum of olefins; 30-46, aromatics; 48, sum of aromatics; 52, acetylene.

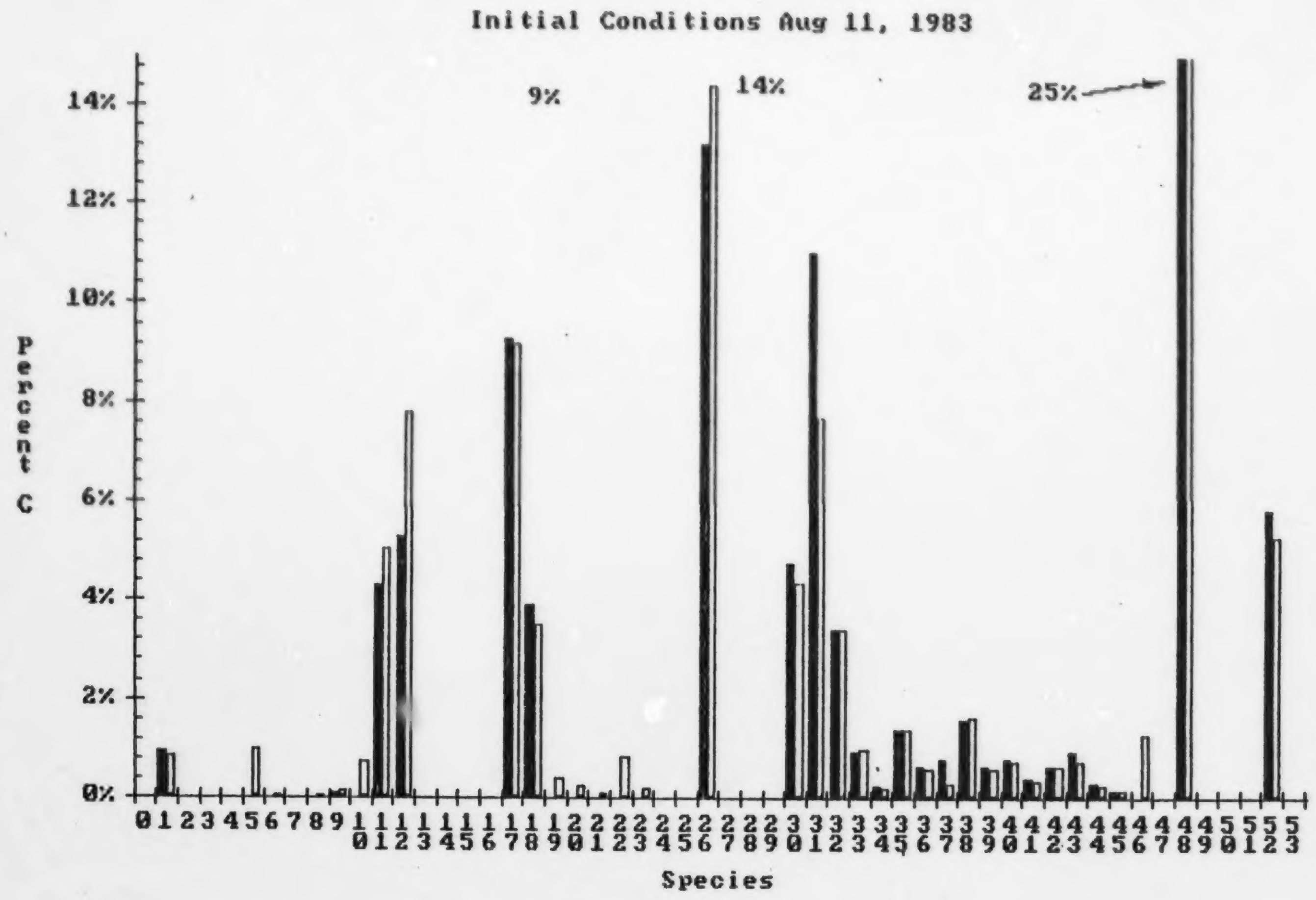


Figure 26.. A comparison of side-by-side injection and analysis in an EKMA-type experiment. Species: 1-10, paraffins; 11, sum of paraffins measured; 12, sum of paraffins with estimated composition; 17-24, olefins; 26, sum of olefins; 30-46, aromatics; 48, sum of aromatics; 52, acetylene.

the measured carbon in each class is listed along with its average carbon number. Next, we estimated the concentration of the "unspeciated carbon" and its carbon number for each class so as to produce an average carbon number in each class that approached the values calculated from the detailed HC analysis. At the same time, the total class fractions had to be resonable compared to other runs and to the detailed dynamometer data. In addition, this division of the "unspeciated carbon" took into account the known deficiencies of particular instruments used, *e.g.* poor measurements of C_4 and C_5 paraffins. Generally, most of the "unspeciated carbon" went into the paraffin class, as it did on the August 11, 1983 spreadsheet

The data in the spreadsheet can be plotted to show the absolute and relative side-to-side agreement. The injection was performed by alternately injecting 3 seconds in the RED side and 1 second in the BLUE side for 45 minutes. Thus the relative distribution of carbon by species and HC class should have been very similar on the two sides. Figure 25 shows the *concentrations* of species and the sum of classes and Figure 26 shows the same data as *percent of total carbon*. These show that the analytical methods worked well over this range of initial conditions.

Summary of Chamber Experiment Initial Conditions

Table 21 lists the initial conditions for all chamber runs performed as part of this program. The column marked "SegFile" indicates whether this experiment has been processed into a segmented data file for model testing use.

Description of Each Experiment

The remaining part of this chapter presents a description of each experiment.

Table 21. Summary of Experimental Initial Concentrations

(all units are ppm or ppmC)

(BLUE data on first line, RED data on second line)

Date	SegFile	Car	Type	NO_x	NO	NO_2	NMHC
June 25, 1982	JN2582	Volare	Direct	0.65	0.60	0.04	0.55
		Volare	Direct	0.66	0.61	0.05	0.55
June 29, 1982	JN2982	Volare	Direct	0.26	0.23	0.03	2.48
		Volare	Direct	0.24	0.22	0.03	2.46
June 30, 1982	JN3082	Volare	Direct	0.33	0.29	0.04	2.84
		Volare	Direct	0.33	0.29	0.04	3.13
July 1, 1982	JL0182	Charger	Direct	0.35	0.33	0.03	3.60
		Charger	Direct	0.37	0.34	0.03	3.53
July 10, 1982		Charger	Direct	0.14	0.10	0.04	1.50
		Charger	Direct	0.14	0.10	0.04	1.50
July 15, 1982	JL1582	Volare	Direct	0.58	0.55	0.03	2.31
		Volare	Direct	0.57	0.54	0.03	2.24
July 20, 1982		Charger	Cryo	0.06	0.02	0.04	1.95
		Charger	Direct	0.06	0.05	0.02	1.05
Aug. 3, 1982	AU0382	Charger	Cryo	0.17	0.10	0.07	1.25
		Charger	Direct	0.46	0.41	0.04	2.45
Aug. 5, 1982		Charger	Cryo	0.38	0.32	0.06	1.40
		Charger	Direct	0.38	0.32	0.06	1.55
Aug. 6, 1982	AU0682	Charger	Cryo	0.36	0.26	0.10	1.07
		Charger	Direct	0.37	0.34	0.03	1.38

Table 21. Summary of Experimental Initial Concentrations, cont.

(all units are ppm or ppmC)

(BLUE data on first line, RED data on second line)

Date	SegFile	Car	Type	NO_x	NO	NO_2	NMHC
Aug. 7, 1982	AU0782	Charger	Cryo	0.29	0.24	0.05	1.45
		Charger	Direct	0.29	0.25	0.05	1.48
Aug. 11, 1982		Charger	Cryo	0.48	0.35	0.13	1.05
		Charger	Direct	0.47	0.35	0.12	1.53
Sept 17, 1982	ST1782	Charger	Cryo	0.25	0.16	0.10	2.42
		Charger	Direct	0.26	0.16	0.10	2.16
Sept 29, 1982	ST2982	Volare	Direct	0.39	0.32	0.07	1.74
		Charger	Direct	0.39	0.32	0.08	1.72
Oct. 6, 1982	OC0682	Charger	Direct	0.47	0.37	0.10	1.96
		Volare	Direct	0.47	0.37	0.10	1.97
June 17, 1983	JN1783	Volare	Direct	0.73	0.57	0.16	2.40
		Charger	Direct	0.72	0.56	0.15	1.10
June 29, 1983	JN2983	Charger	Direct	0.16	0.12	0.04	0.80
		Charger	Direct	0.15	0.11	0.04	2.50
July 2, 1983	JL0283	Volare	Direct	0.18	0.16	0.02	1.70
		Charger	Direct	0.18	0.16	0.01	1.64
July 8, 1983	JL0883	Volare	Direct	0.37	0.31	0.06	1.69
		Charger	Direct	0.37	0.31	0.06	1.73
July 15, 1[illegible]	JL1583	Charger	Direct	0.35	0.31	0.05	2.25
		Charger	Direct	0.36	0.31	0.05	2.19

Table 21. Summary of Experimental Initial Concentrations, cont.

(all units are ppm or ppmC)

(BLUE data on first line, RED data on second line)

Date	SegFile	Car	Type	NO_x	NO	NO_2	NMHC
July 22, 1983		Charger	Direct	0.27	0.21	0.07	1.86
		Charger	Direct	0.27	0.21	0.06	1.81
July 25, 1983	JL2583	SynAuto		0.22	0.19	0.04	2.85
		SynAuto		0.24	0.20	0.04	2.96
July 28, 1983	JL2883	Charger	Direct	0.29	0.26	0.04	2.52
		Charger	Direct	0.29	0.26	0.04	2.50
Aug. 11, 1983	AU1183	Volare	Direct	0.22	0.19	0.03	0.68
		Volare	Direct	0.22	0.19	0.04	2.15
Sept 2, 1983		SynAuto		0.28	0.23	0.04	2.39
		Charger	Direct	0.28	0.24	0.04	3.00
Sept 9, 1983	ST0983	SynAuto		0.30	0.27	0.03	2.06
		Charger	Direct	0.30	0.27	0.02	2.80
Sept 20, 1983		SynAuto		0.25	0.24	0.01	2.40
		Charger	Direct	0.25	0.23	0.02	2.94
Oct. 4, 1983	OC0483	SynAuto		0.25	0.21	0.04	2.19
		Charger	Direct	0.25	0.22	0.04	2.59
Oct. 7, 1983	OC0783	SynAuto		0.35	0.31	0.04	2.69
		SynUrb		0.33	0.29	0.04	2.65
Oct 19, 1983	OC1983	Volare	Direct	0.84	0.76	0.07	0.35
		Charger	Direct	0.83	0.76	0.08	0.35
Oct 28, 1983	OC2883	Charger	Direct	0.26	0.23	0.03	2.37
		Volare	Direct	0.28	0.25	0.03	2.40
Nov 2, 1983	NO0283	Charger	Direct	0.27	0.25	0.02	1.50
		Volare	Direct	0.27	0.25	0.02	1.56

June 25, 1982

Matched Direct Injections from 1979 Plymouth Volare

INITIAL CONDITIONS:	BLUE	RED
NO	0.604	0.612
NO2	0.044	0.046
NMHC	0.550	0.550
CO (ESTIMATED) @	7.500	7.550

@ THE CO CONCENTRATION WAS ESTIMATED BECAUSE THE CO INSTRUMENT WAS NOT FUNCTIONING UNTIL 957.

SUNLIGHT AND WEATHER:	2.0/10.0	2.0/10.0
TEMPERATURE F:	65.0	89.0

INSTRUMENTS USED:
1: CARLE I GC
2: CARLE II GC
3: PERKIN ELMER 900 GC
4: BECKMAN 6800 THC/CH4
5: CEA FORMALDEHYDE
6: VARIAN GC

DATA EXCEPTIONS: NONE

CHAMBER CONDITIONS:
1: GREATER THAN 6 HOURS VENTING
2: NO DRYING WAS PERFORMED
3: NO CONDENSATION WAS OBSERVED

SPECIAL PROBLEMS OR CONCERNS:
1: NONE

EXPERIMENT STARTS:	0548
INITIAL CONDITIONS ESTABLISHED:	0548
EXPERIMENTS ENDS:	1800

RUN QUALITY INDEX:	8.2/10.0

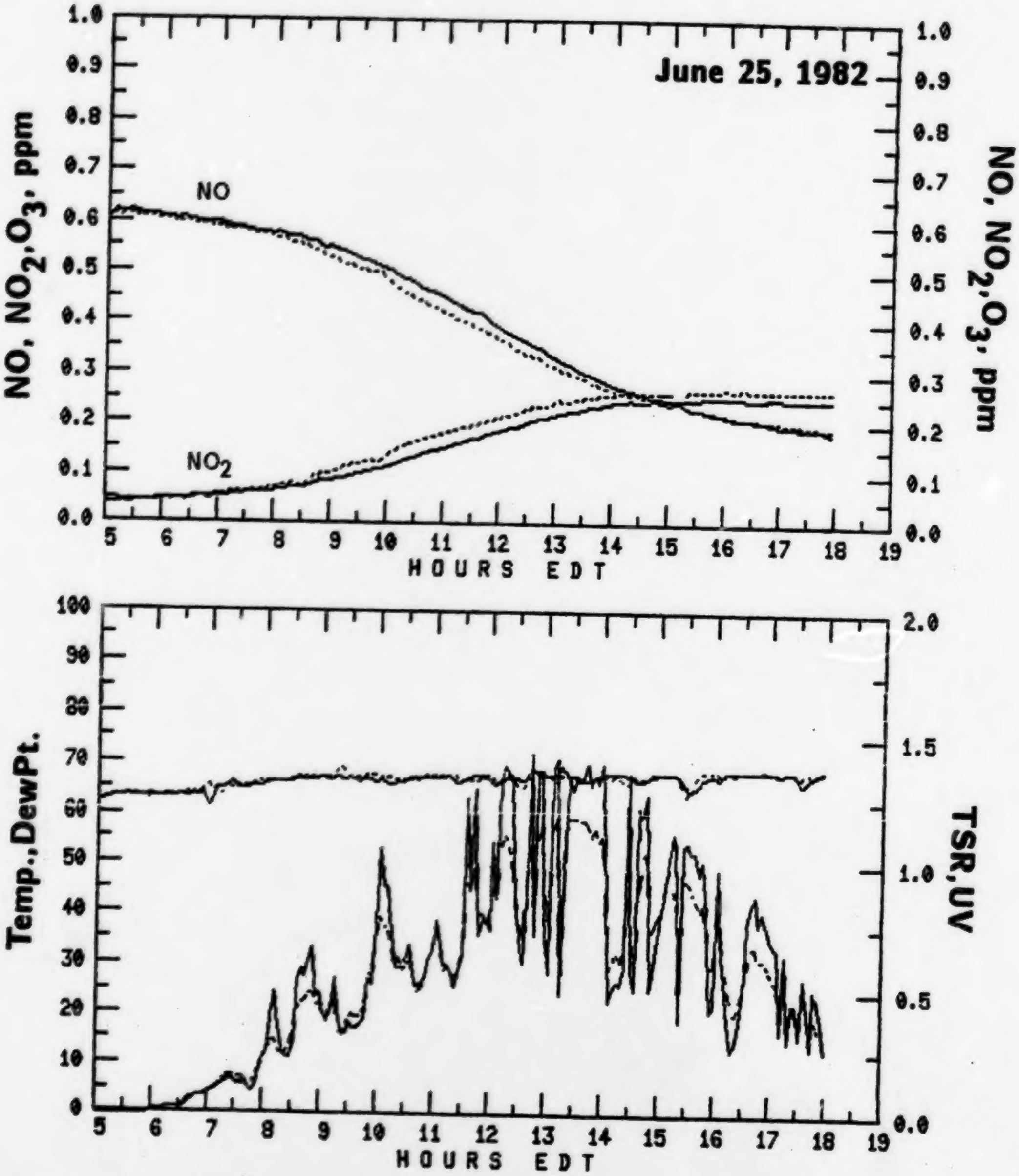


Figure D1. TOP: Plymouth Volare, direct injection , NMHC= 0.55 ppmC, (dashed lines); Plymouth Volare, direct injection, NMHC= 0.55 ppmC, (solid lines).
BOTTOM: Chamber air temperature and dew point; ambient total solar and ultraviolet radiation;

Initial Conditions for June 25, 1982

			PV/76/Dir BLUE			PV/76/Dir RED		
	Cnum	Split *	PPMC	%C	PPMV	RED	%C	PPMV
PARAFFINS								
ethane	2		0.021	3.82	0.011	0.019	3.45	0.010
propane	3		ND	NA	ND	ND	NA	ND
n-butane	4		0.021	3.82	0.005	0.017	3.09	0.004
i-butane	4		NM	NA	NM	NM	NA	NM
i-pentane	5		ND	NA	ND	ND	NA	ND
n-pentane	5		ND	NA	ND	ND	NA	ND
2-me-pentane	6		ND	NA	ND	ND	NA	ND
trime-pentanes	8		NM	NA	NM	NM	NA	NM
octane	8		NM	NA	NM	NM	NA	NM
C6 unk(C1G)	6		ND	NA	ND	ND	NA	ND
Sub-total			0.042	7.64	0.016	0.036	6.55	0.014
OLEFINS								
ethylene	2		0.105	19.09	0.053	0.108	19.64	0.054
propylene	3		0.059	10.73	0.020	0.050	9.09	0.017
1-butene	4		NM	NA	NM	NM	NA	NM
c-2-butene	4		NM	NA	NM	NM	NA	NM
t-2-butene	4		NM	NA	NM	NM	NA	NM
1,3butadiene	4		NM	NA	NM	NM	NA	NM
2-me-1-butene	5		ND	NA	ND	ND	NA	ND
2-me-2-butene	5		ND	NA	ND	ND	NA	ND
Sub-total			0.164	29.82	0.072	0.158	28.73	0.071

AROMATICS								
benzene	6		0.082	14.91	0.014	0.090	16.36	0.015
toluene	7		0.062	11.27	0.009	0.063	11.45	0.009
mp-xylene	8		0.044	8.00	0.006	0.046	8.38	0.006
et-benzenes	8		0.014	2.55	0.002	0.029	5.27	0.004
pro-benzenes	9		ND	NA	ND	ND	NA	ND
o-xylene	8		0.020	3.64	0.003	0.019	3.45	0.002
135-C3-benzene	9		0.026	4.73	0.003	0.026	4.73	0.003
123-C3-benzene	9		ND	NA	ND	ND	NA	ND
124-C3-benzene	9		ND	NA	ND	ND	NA	ND
dimeet-benzene	10		ND	NA	ND	ND	NA	ND
m-eth-toluene	9		0.016	2.91	0.002	0.013	2.36	0.001
o-eth-toluene	9		ND	NA	ND	ND	NA	ND
styrene	8		0.011	2.00	0.001	0.009	1.64	0.001
napthalene	10		0.019	3.45	0.002	0.017	3.09	0.002
2me-napthalene	11		ND	NA	ND	ND	NA	ND
1me-mapthalene	11		ND	NA	ND	ND	NA	ND
others	10	4	0.032	5.82	0.003	0.030	5.45	0.003
Sub-total			0.326	59.27	0.043	0.342	62.18	0.046
ACETYLENE								
acetylene	2		0.058	10.55	0.029	0.057	10.36	0.029
TOTAL MEASURED SPECIES			0.590	107.27	0.160	0.593	107.82	0.159
Unspeciated Carbon			-0.040	-7.27		-0.043	-7.82	
FINAL NMHC			0.550			0.550		

```
#####################################################|###########################
                                                     |
SUMMARY                                              |
                          PPMC      %C      Car Num  |  PPMC      %C      Car Num
                                                     |
     Meas PAR             0.042     7.64     2.67    |  0.036     6.55     2.62
     Est  PAR             0.000     0.00     0.00    |  0.000     0.00     0.00
                       ------------------------------|---------------------------
     TOT  PAR          5  0.042     7.64     5.15    |  0.036     6.55     5.15
                                                     |
                                                     |
     Meas OLE             0.164    29.82     2.27    |  0.158    28.73     2.24
      Est OLE             0.000     0.00     0.00    |  0.000     0.00     0.00
                       ------------------------------|---------------------------
      TOT OLE          5  0.164    29.82     2.55    |  0.158    28.73     2.55
                                                     |
                                                     |
     Meas ARO             0.326    59.27     7.51    |  0.342    62.18     7.45
      Est ARO             0.000     0.00     0.00    |  0.000     0.00     0.00
                       ------------------------------|---------------------------
                       5  0.326    59.27     7.85    |  0.342    62.18     7.85
                                                     |
     Meas ACE             0.058    10.55     2.00    |  0.057    10.36     2.00
                       ------------------------------|---------------------------
      TOT ACE             0.058    10.55     2.00    |  0.057    10.36     2.00
                                                     |
--------------         ------------------------------|---------------------------
--------------         ------------------------------|---------------------------
      Spec HC             0.590   107.27             |  0.593   107.82
    Unspec HC             0.000     0.00             |  0.000     0.00
                       --------------------          |--------------------
     TOT NMHC             0.590   107.27             |  0.593   107.82
```

June 29, 1982

Matched Direct Injections from 1979 Plymouth Volare

INITIAL CONDITIONS:	BLUE	RED
NO	0.232	0.219
NO2	0.028	0.025
NMHC	2.483	2.464
CO	55.335	59.964

	MORN	AFTERNOON
SUNLIGHT AND WEATHER:	2.5/10.0	3.0/10.0
TEMPERATURE F:	71	95

INSTRUMENTS USED:
1: CARLE I GC
2: CARLE II GC
3: PERKIN ELMER 900 GC
4: BECKMAN 6800 THC/CH4
5: CEA FORMALDEHYDE
6: VARIAN GC

DATA EXCEPTIONS: MISSING SOME MORNING HC DATA.

CHAMBER CONDITIONS:
1: GREATER THAN 6 HOURS DRYING
2: SOME CONDENSATION WAS OBSERVED IN BOTH SIDES.

SPECIAL PROBLEMS OR CONCERNS:
1: NONE

EXPERIMENT STARTS: 0600
INITIAL CONDITIONS ESTABLISHED: 0513
EXPERIMENTS ENDS: 1607

RUN QUALITY INDEX: 8.13/10.0

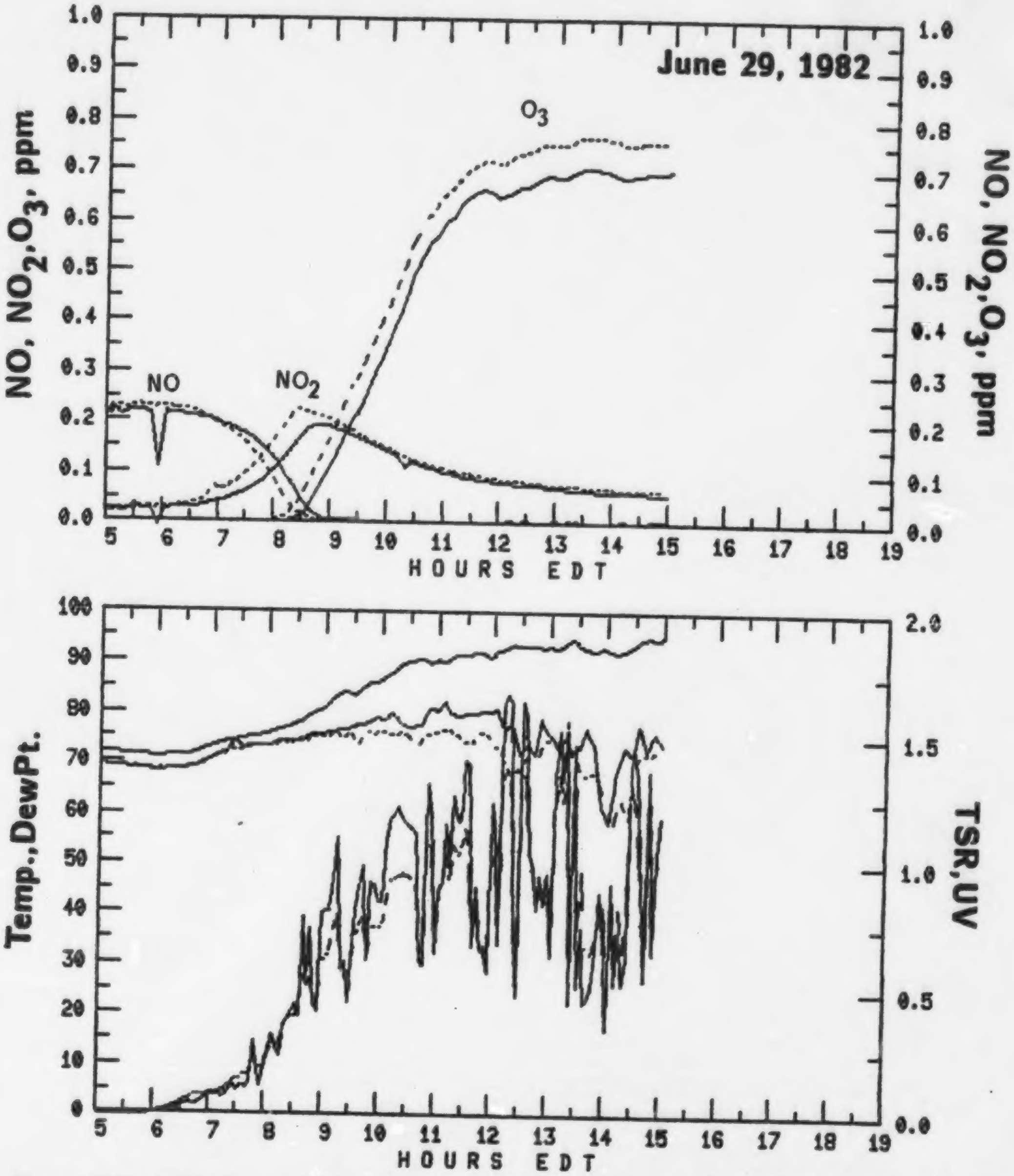


Figure D2. TOP: Plymouth Volare, direct injection , NMHC= 2.48 ppmC, (dashed lines); Plymouth Volare, direct injection, NMHC= 2.46 ppmC, (solid lines).
BOTTOM: Chamber air temperature and dew point; ambient total solar and ultraviolet radiation;

Initial Conditions for June 29, 1982

			PV/76/Dir BLUE			PV/76/Dir RED		
	Cnum	Split *	PPMC	%C	PPMV	RED	%C	PPMV
PARAFFINS								
ethane	2		0.033	1.33	0.017	0.029	1.18	0.015
propane	3		ND	NA	ND	ND	NA	ND
n-butane	4		NM	NA	NM	NM	NA	NM
i-butane	4		NM	NA	NM	NM	NA	NM
i-pentane	5		ND	NA	ND	ND	NA	ND
n-pentane	5		ND	NA	ND	ND	NA	ND
2-me-pentane	6		ND	NA	ND	ND	NA	ND
trime-pentanes	8		NM	NA	NM	NM	NA	NM
octane	8		NM	NA	NM	NM	NA	NM
C6 unk(C1G)	6		ND	NA	NDO	ND	NA	ND
Sub-total			0.033	1.33	0.017	0.029	1.18	0.015
OLEFINS								
ethylene	2		0.300	12.08	0.150	0.300	12.18	0.150
propylene	3		0.151	6.08	0.050	0.151	6.13	0.050
1-butene	4		NM	NA	NM	NM	NA	NM
c-2-butene	4		NM	NA	NM	NM	NA	NM
t-2-butene	4		NM	NA	NM	NM	NA	NM
1,3butadiene	4		NM	NA	NM	NM	NA	NM
2-me-1-butene	5		ND	NA	ND	ND	NA	ND
2-me-2-butene	5		ND	NA	ND	ND	NA	ND
Sub-total			0.451	18.16	0.200	0.451	18.30	0.200

AROMATICS								
benzene	6		0.281	11.32	0.047	0.280	11.36	0.047
toluene	7		0.255	10.27	0.036	0.268	10.88	0.038
mp-xylene	8		0.163	6.56	0.020	0.160	6.49	0.020
et-benzenes	8		0.046	1.85	0.006	0.043	1.75	0.005
pro-benzenes	9		ND	NA	ND	ND	NA	ND
o-xylene	8		0.067	2.70	0.008	0.070	2.84	0.009
135-C3-benzene	9		0.029	1.17	0.003	0.024	0.97	0.003
123-C3-benzene	9		0.021	0.85	0.002	0.020	0.81	0.002
124-C3-benzene	9		0.090	3.62	0.010	0.090	3.65	0.010
dimeet-benzene	10		0.054	2.17	0.005	0.050	2.03	0.005
m-eth-toluene	9		0.050	2.01	0.006	0.047	1.91	0.005
o-eth-toluene	9		ND	NA	ND	ND	NA	ND
styrene	8		0.048	1.93	0.006	0.042	1.70	0.005
napthalene	10		0.075	3.02	0.008	0.070	2.84	0.007
2me-napthalene	11		ND	NA	ND	ND	NA	ND
1me-mapthalene	11		ND	NA	ND	ND	NA	ND
others	10	4	0.111	4.47	0.011	0.094	3.81	0.009
Sub-total			1.290	51.95	0.169	1.258	51.06	0.166
ACETYLENE								
acetylene	2		0.321	12.93	0.161	0.311	12.62	0.156
TOTAL MEASURED SPECIES			2.095	84.37	0.546	2.049	83.16	0.536
Unspeciated Carbon			0.388	15.63		0.415	16.84	
FINAL NMHC			2.483			2.464		

```
#####################################################|##########################
                                                     |
SUMMARY                                              |
                            PPMC       %C    Car Num | PPMC       %C    Car Num
                                                     |
     Meas PAR                0.033     1.33     2.00 |  0.029     1.18     2.00
     Est  PAR                0.400    16.11     5.92 |  0.400    16.23     5.81
                          ---------------------------|---------------------------
     TOT  PAR           5    0.433    17.44     5.15 |  0.429    17.41     5.15
                                                     |
                                                     |
     Meas OLE                0.451    18.16     2.25 |  0.451    18.30     2.25
      Est OLE                0.000     0.00     0.00 |  0.000     0.00     0.00
                          ---------------------------|---------------------------
      TOT OLE           5    0.451    18.16     2.55 |  0.451    18.30     2.55
                                                     |
                                                     |
     Meas ARO                1.290    51.95     7.64 |  1.258    51.06     7.59
      Est ARO                0.000     0.00     0.00 |  0.000     0.00     0.00
                          ---------------------------|---------------------------
                        5    1.290    51.95     7.85 |  1.258    51.06     7.85
                                                     |
     Meas ACE                0.321    12.93     2.00 |  0.311    12.62     2.00
                          ---------------------------|---------------------------
      TOT ACE                0.321    12.93     2.00 |  0.311    12.62     2.00
                                                     |
--------------            ---------------------------|---------------------------
--------------            ---------------------------|---------------------------
      Spec HC                2.095    84.37          |  2.049    83.16
    Unspec HC                0.400    16.11          |  0.400    16.23
                          ------------------         |------------------
     TOT NMHC                2.495   100.48          |  2.449    99.39
```

June 30, 1982

Matched Direct Injections from 1979 Plymouth Volare

INITIAL CONDITIONS:	BLUE	RED
NO	0.292	0.294
NO2	0.035	0.035
NMHC	3.170	3.126
CO	64.887	66.461

	MORN	AFTERNOON
SUNLIGHT AND WEATHER:	7.3/10.0	7.0/10.0
TEMPERATURE F:	68.0	94.0

INSTRUMENTS USED:
1: CARLE I GC
2: CARLE II GC
3: PERKIN ELMER 900 GC
4: BECKMAN 6800 THC/CH4
5: CEA FORMALDEHYDE
6: VARIAN GC

DATA EXCEPTIONS: PROPYLENE AFTER INITIAL CONDITIONS

CHAMBER CONDITIONS:
1: GREATER THAN 6 HOURS VENTING
2: NO DRYING WAS PERFORMED
3: SLIGHT CONDENSATION WAS OBSERVED IN BOTH SIDES

SPECIAL PROBLEMS OR CONCERNS: NONE

EXPERIMENT STARTS: 0530
INITIAL CONDITIONS ESTABLISHED: 0527
EXPERIMENTS ENDS: 1530

RUN QUALITY INDEX: 9.4/10.0

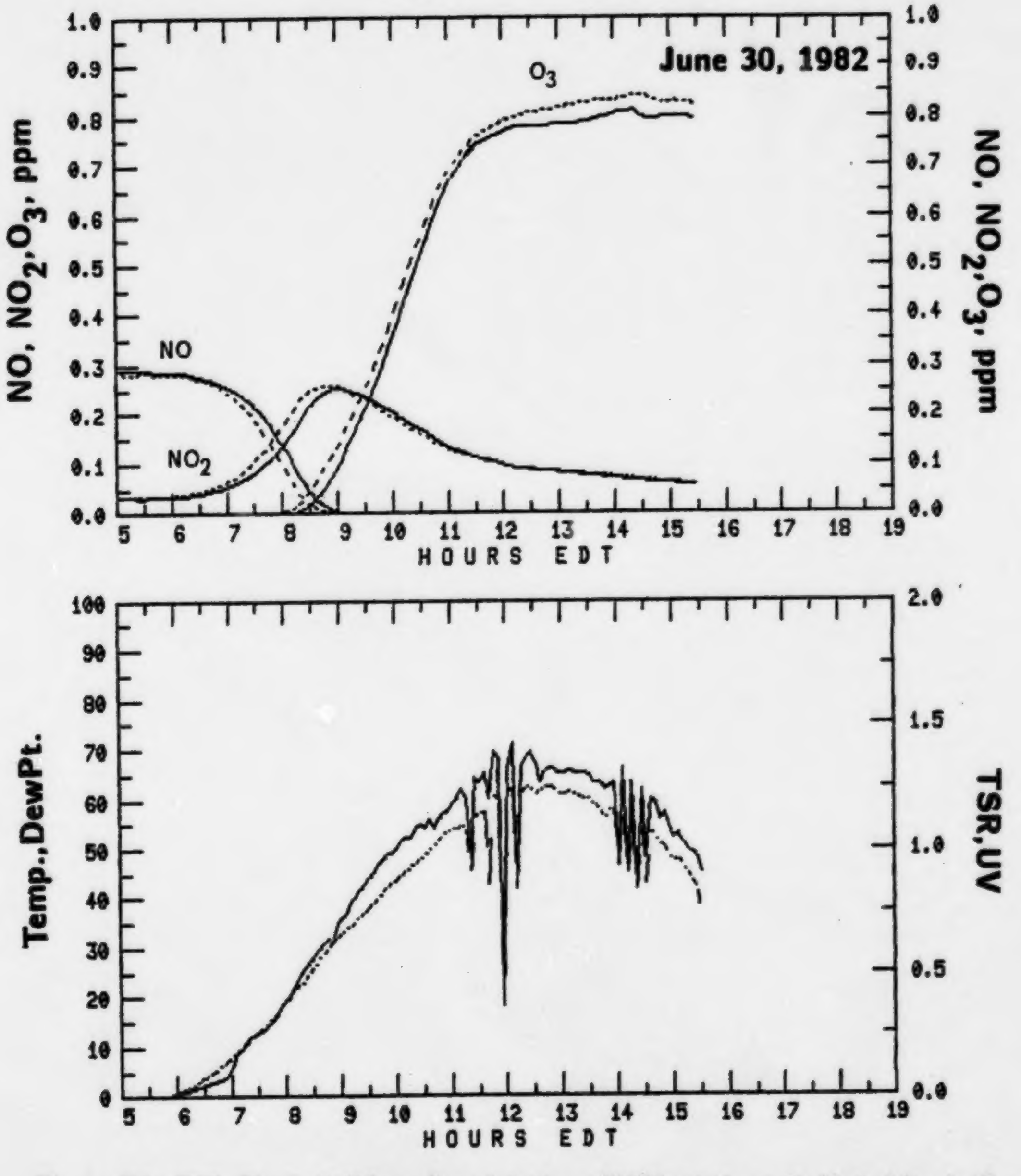


Figure D3. TOP: Plymouth Volare, direct injection , NMHC= 3.13 ppmC, (dashed lines); Plymouth Volare, direct injection, NMHC= 2.84 ppmC, (solid lines).
BOTTOM: Chamber air temperature and dew point; ambient total solar and ultraviolet radiation;

Initial Conditions for June 30, 1982

			PV/76/Dir			PV/76/Dir		
			BLUE			RED		
	Cnum	Split *	PPMC	%C	PPMV	RED	%C	PPMV
PARAFFINS								
ethane	2		0.049	1.55	0.025	0.048	1.54	0.024
propane	3		ND	NA	ND	ND	NA	ND
n-butane	4		0.232	7.32	0.058	0.246	7.87	0.062
i-butane	4		NM	NA	NM	NM	NA	NM
i-pentane	5		T	NA	T	T	NA	T
n-pentane	5		ND	NA	ND	ND	NA	ND
2-me-pentane	6		T	NA	T	T	NA	T
trime-pentanes	8		NM	NA	NM	NM	NA	NM
octane	8		NM	NA	NM	NM	NA	NM
C6 unk(C1G)	6		ND	NA	ND	ND	NA	ND
Sub-total			0.281	8.86	0.083	0.294	9.40	0.086
OLEFINS								
ethylene	2		0.458	14.45	0.229	0.472	15.10	0.236
propylene	3		0.185	5.84	0.062	0.182	5.82	0.061
1-butene	4		NM	NA	NM	NM	NA	NM
c-2-butene	4		NM	NA	NM	NM	NA	NM
t-2-butene	4		NM	NA	NM	NM	NA	NM
1,3butadiene	4		NM	NA	NM	NM	NA	NM
2-me-1-butene	5		ND	NA	ND	ND	NA	ND
2-me-2-butene	5		T	NA	T	T	NA	T
Sub-total			0.643	20.28	0.291	0.654	20.92	0.297

AROMATICS								
benzene	6		0.314	9.91	0.052	0.320	10.24	0.053
toluene	7		0.334	10.54	0.048	0.328	10.49	0.047
mp-xylene	8		0.226	7.13	0.028	0.213	6.81	0.027
et-benzenes	8		0.050	1.58	0.006	0.051	1.63	0.006
pro-benzenes	9		0.008	0.25	0.001	0.012	0.38	0.001
o-xylene	8		0.080	2.52	0.010	0.078	2.50	0.010
135-C3-benzene	9		0.029	0.91	0.003	0.148	4.73	0.016
123-C3-benzene	9		0.023	0.73	0.003	0.019	0.61	0.002
124-C3-benzene	9		0.101	3.19	0.011	0.097	3.10	0.011
dimeet-benzene	10		0.070	2.21	0.007	0.062	1.98	0.006
m-eth-toluene	9		0.058	1.83	0.006	0.075	2.40	0.008
o-eth-toluene	9		0.020	0.63	0.002	0.017	0.54	0.002
styrene	8		0.055	1.74	0.007	0.059	1.89	0.007
napthalene	10		0.091	2.87	0.009	0.083	2.66	0.008
2me-napthalene	11		0.033	1.04	0.003	0.031	0.99	0.003
1me-napthalene	11		0.014	0.44	0.001	0.015	0.48	0.001
others	10	4	0.196	6.18	0.020	0.188	6.01	0.019
Sub-total			1.702	53.69	0.218	1.796	57.45	0.229
ACETYLENE								
acetylene	2		0.389	12.27	0.195	0.380	12.16	0.190
TOTAL MEASURED SPECIES			3.015	95.11	0.786	3.124	99.94	0.801
Unspeciated Carbon			0.155	4.89		0.002	0.06	
FINAL NMHC			3.170			3.126		

```
                                                        |
                                                        |

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                                                        |
SUMMARY                                                 |
                              PPMC       %C     Car Num | PPMC        %C      Car Num
                                                        |
     Meas PAR                  0.281      8.86     3.41 |    0.294      9.40      3.44
     Est  PAR                  0.000      0.00     0.00 |    0.000      0.00      0.00
                            ----------------------------|-----------------------------
     TOT  PAR              5   0.281      8.86     5.15 |    0.294      9.40      5.15
                                                        |
                                                        |
     Meas OLE                  0.643     20.28     2.21 |    0.654     20.92      2.20
      Est OLE                  0.000      0.00     0.00 |    0.000      0.00      0.00
                            ----------------------------|-----------------------------
      TOT OLE              5   0.643     20.28     2.55 |    0.654     20.92      2.55
                                                        |
                                                        |
     Meas ARO                  1.702     53.69     7.81 |    1.796     57.45      7.85
      Est ARO                  0.000      0.00     0.00 |    0.000      0.00      0.00
                            ----------------------------|-----------------------------
                           5   1.702     53.69     7.85 |    1.796     57.45      7.85
                                                        |
     Meas ACE                  0.389     12.27     2.00 |    0.380     12.16      2.00
                            ----------------------------|-----------------------------
      TOT ACE                  0.389     12.27     2.00 |    0.380     12.16      2.00
                                                        |
---------------             ----------------------------|-----------------------------
---------------             ----------------------------|-----------------------------
      Spec HC                  3.015     95.11          |    3.124     99.94
    Unspec HC                  0.000      0.00          |    0.000      0.00
                            -------------------         |--------------------
     TOT NMHC                  3.015     95.11          |    3.124     99.94
```

July 1, 1982

Matched Direct Injections from 1972 Dodge Charger

INITIAL CONDITIONS:	BLUE	RED
NO	0.325	0.340
NO2	0.027	0.029
NMHC	3.599	3.534
CO	74.825	72.991

	MORN	AFTERNOON
SUNLIGHT AND WEATHER:	8.25/10.0	9.0/10.0
TEMPERATURE F:	60.0	85.0

INSTRUMENTS USED:
1: CARLE I GC
2: CARLE II GC
3: PERKIN ELMER 900 GC
4: BECKMAN 6800 THC/CH4
5: CEA FORMALDEHYDE
6: VARIAN GC

DATA EXCEPTIONS: NONE

CHAMBER CONDITIONS:
1: LESS THAN 7 HOURS OF VENTING.
2: NO DRYING WAS PERFORMED.
3: SOME CONDENSATION WAS OBSERVED IN BOTH SIDES.

SPECIAL PROBLEMS OR CONCERNS: NONE

EXPERIMENT STARTS:	0556
INITIAL CONDITIONS ESTABLISHED:	0540
EXPERIMENTS ENDS:	1740

RUN QUALITY INDEX: 9.4/10.0

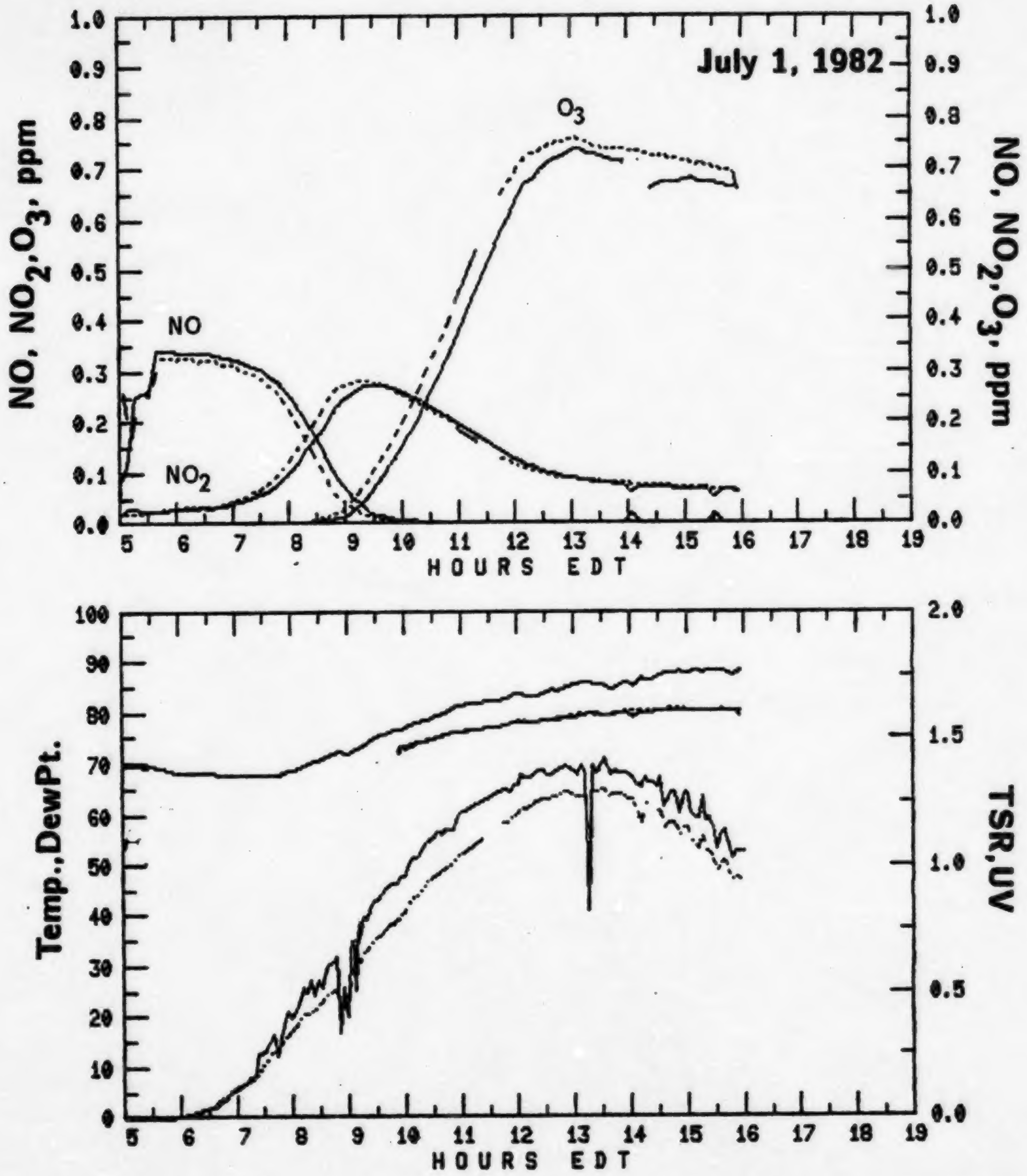


Figure D4. TOP: Dodge Charger, direct injection , NMHC= 3.60 ppmC, (dashed lines); Dodge Charger, direct injection, NMHC= 3.53 ppmC, (solid lines).
BOTTOM: Chamber air temperature and dew point; ambient total solar and ultraviolet radiation;

Initial Conditions for July 1, 1982

	Cnum	Split *	DC/76/Dir BLUE PPMC	%C	PPMV	DC/76/Dir RED RED	%C	PPMV
PARAFFINS								
ethane	2		0.062	1.72	0.031	0.064	1.81	0.032
propane	3		0.085	2.36	0.028	0.085	2.41	0.028
n-butane	4		0.252	7.00	0.063	0.238	6.73	0.060
i-butane	4		NM	NA	NM	NM	NA	NM
i-pentane	5		0.020	0.56	0.004	0.020	0.57	0.004
n-pentane	5		0.010	0.28	0.002	0.010	0.28	0.002
2-me-pentane	6		0.070	1.94	0.012	0.070	1.98	0.012
trime-pentanes	8		NM	NA	NM	NM	NA	NM
octane	8		NM	NA	NM	NM	NA	NM
C6 unk(C1G)	6		ND	NA	ND	ND	NA	ND
Sub-total			0.499	13.86	0.140	0.487	13.78	0.138
OLEFINS								
ethylene	2		0.640	17.78	0.320	0.611	17.29	0.306
propylene	3		0.215	5.97	0.072	0.180	5.09	0.060
1-butene	4		NM	NA	NM	NM	NA	NM
c-2-butene	4		NM	NA	NM	NM	NA	NM
t-2-butene	4		NM	NA	NM	NM	NA	NM
1,3butadiene	4		NM	NA	NM	NM	NA	NM
2-me-1-butene	5		ND	NA	ND	ND	NA	ND
2-me-2-butene	5		0.030	0.83	0.006	0.030	0.85	0.006
Sub-total			0.885	24.59	0.398	0.821	23.23	0.372

AROMATICS								
benzene	6		0.280	7.78	0.047	0.280	7.92	0.047
toluene	7		0.339	9.42	0.048	0.322	9.11	0.046
mp-xylene	8		0.172	4.78	0.022	0.153	4.33	0.019
et-benzenes	8		0.053	1.47	0.007	0.049	1.39	0.006
pro-benzenes	9		ND	NA	ND	ND	NA	ND
o-xylene	8		0.074	2.06	0.009	0.066	1.87	0.008
135-C3-benzene	9		0.029	0.81	0.003	0.029	0.82	0.003
123-C3-benzene	9		0.021	0.58	0.002	0.015	0.42	0.002
124-C3-benzene	9		0.101	2.81	0.011	0.076	2.15	0.008
dimeet-benzene	10		0.093	2.58	0.009	0.073	2.07	0.007
m-eth-toluene	9		0.052	1.44	0.006	0.046	1.30	0.005
o-eth-toluene	9		ND	NA	ND	ND	NA	ND
styrene	8		0.070	1.94	0.009	0.062	1.75	0.008
napthalene	10		0.094	2.61	0.009	0.087	2.46	0.009
2me-napthalene	11		ND	NA	ND	ND	NA	ND
1me-mapthalene	11		ND	NA	ND	ND	NA	ND
others	10	4	0.144	4.00	0.014	0.117	3.31	0.012
Sub-total			1.522	42.29	0.197	1.375	38.91	0.180
ACETYLENE								
acetylene	2		0.722	20.06	0.361	0.721	20.40	0.361
TOTAL MEASURED SPECIES			3.628	100.81	1.096	3.404	96.32	1.050
Unspeciated Carbon			-0.029	-0.81		0.130	3.68	
FINAL NMHC			3.599			3.534		

```
                                                            |
                                                            |
#######################################################|###########################
                                                            |
SUMMARY                                                     |
                              PPMC       %C      Car Num |  PPMC        %C      Car Num
                                                            |
     Meas PAR                 0.499     13.86      3.56 |  0.487     13.78      3.54
     Est  PAR                 0.000      0.00      0.00 |  0.000      0.00      0.00
                           ----------------------------|---------------------------
     TOT  PAR           5    0.499     13.86      5.15 |  0.487     13.78      5.15
                                                            |
                                                            |
     Meas OLE                 0.885     24.59      2.23 |  0.821     23.23      2.21
      Est OLE                 0.000      0.00      0.00 |  0.000      0.00      0.00
                           ----------------------------|---------------------------
      TOT OLE           5    0.885     24.59      2.55 |  0.821     23.23      2.55
                                                            |
                                                            |
     Meas ARO                 1.522     42.29      7.73 |  1.375     38.91      7.64
      Est ARO                 0.000      0.00      0.00 |  0.000      0.00      0.00
                           ----------------------------|---------------------------
                        5    1.522     42.29      7.85 |  1.375     38.91      7.85
                                                            |
     Meas ACE                 0.722     20.06      2.00 |  0.721     20.40      2.00
                           ----------------------------|---------------------------
      TOT ACE                 0.722     20.06      2.00 |  0.721     20.40      2.00
                                                            |
--------------             ----------------------------|---------------------------
--------------             ----------------------------|---------------------------
      Spec HC                 3.628    100.81            |  3.404     96.32
    Unspec HC                 0.000      0.00            |  0.000      0.00
                           ------------------          |------------------
     TOT NMHC                 3.628    100.81            |  3.404     96.32
```

July 10, 1982

Matched Direct Injections from 1972 Dodge Charger

INITIAL CONDITIONS	BLUE	RED
NO	0.12	0.12
NO2	0.05	0.03
NMHC	1.5	1.5
CO	13.	13.

	MORN	AFTERNOON
SUNLIGHT AND WEATHER:	1.5/10.0	3.0/10.0
TEMPERATURE F:	72.0	88.0

INSTRUMENTS USED:
1: CARLE I GC
2: CARLE II GC
3: PERKIN ELMER 900 GC
4: BECKMAN 6800 THC/CH4
5: CEA FORMALDEHYDE
6: VARIAN GC

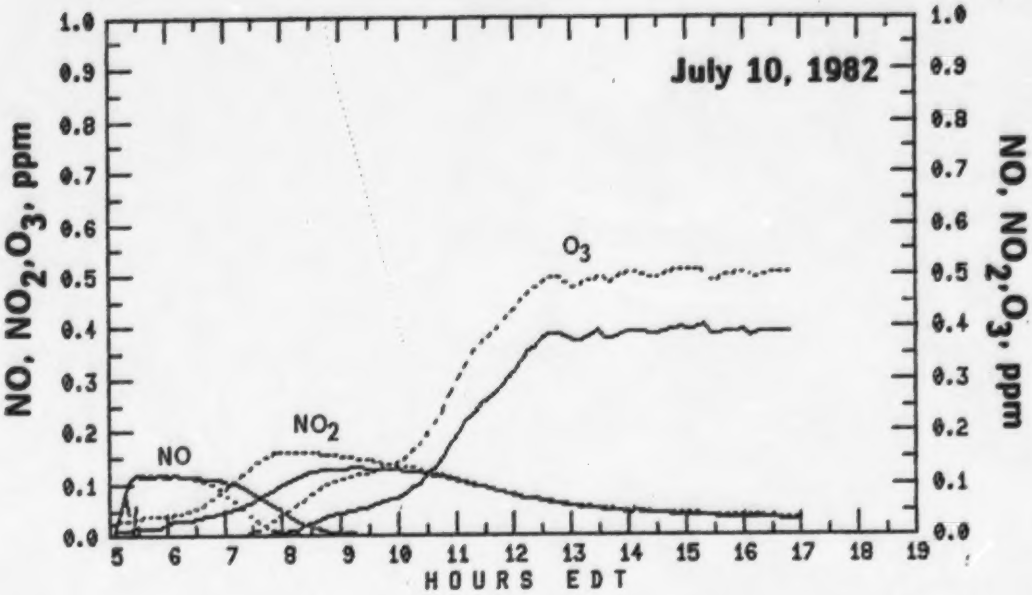
DATA EXCEPTIONS: TSR AND TEMPERATURE DATA.

CHAMBER CONDITIONS:
1: MORE THAN 24 HOURS VENTING BEFORE RUN.
2: DRYING PERFORMED; NO CONDENSATION OBSERVED.

SPECIAL PROBLEMS OR CONCERNS:
1: CONDENSATION ON OUTSIDE OF CHAMBERS.
2: VERY POOR SUN. DATA PLOT NOT AVAILABLE
3: SOME UNCERTAINTY IN INITIAL NMHC.
4: EXPERIMENT NOT TO BE PROCESSED.

EXPERIMENT STARTS:	0555
INITIAL CONDITIONS ESTABLISHED:	0530
EXPERIMENTS ENDS:	1759

RUN QUALITY INDEX: 4.0/10.0



DATA MISSING

Figure D5. TOP: Dodge Charger, direct injection , NMHC= 1.5 ppmC, (dashed lines); Dodge Charger, direct injection, NMHC= 1.5 ppmC, (solid lines).

July 15, 1982

Direct Matched Injections from 1979 Plymouth Volare Toluene Added to BLUE Side m-Xylene Added to RED Side

INITIAL CONDITIONS	BLUE	RED
NO	0.545	0.537
NO2	0.031	0.029
NMHC	1.88	1.71
TOLUENE	0.431	--
M-XYLENE	--	0.527

	MORN	AFTERNOON
SUNLIGHT AND WEATHER:	6.5/10.0	3.0/10.0
TEMPERATURE F:	73.0	86.0

INSTRUMENTS USED:
1: CARLE I GC
2: CARLE II GC
3: PERKIN ELMER 900 GC
4: BECKMAN 6800 THC/CH4
5: CEA FORMALDEHYDE
6: VARIAN GC

DATA EXCEPTIONS: DEWPOINT DATA;

CHAMBER CONDITIONS:
1: 7 HOURS VENTING BEFORE RUN;
2: DRYING PERFORMED; NO CONDENSATION OBSERVED.

SPECIAL PROBLEMS OR CONCERNS:
1: CONDENSATION ON OUTSIDE OF CHAMBERS.
2: THE SUN WAS VERY POOR.

EXPERIMENT STARTS: 0548
INITIAL CONDITIONS ESTABLISHED: 0548
EXPERIMENTS ENDS: 1759

RUN QUALITY INDEX: 8.79/10.0

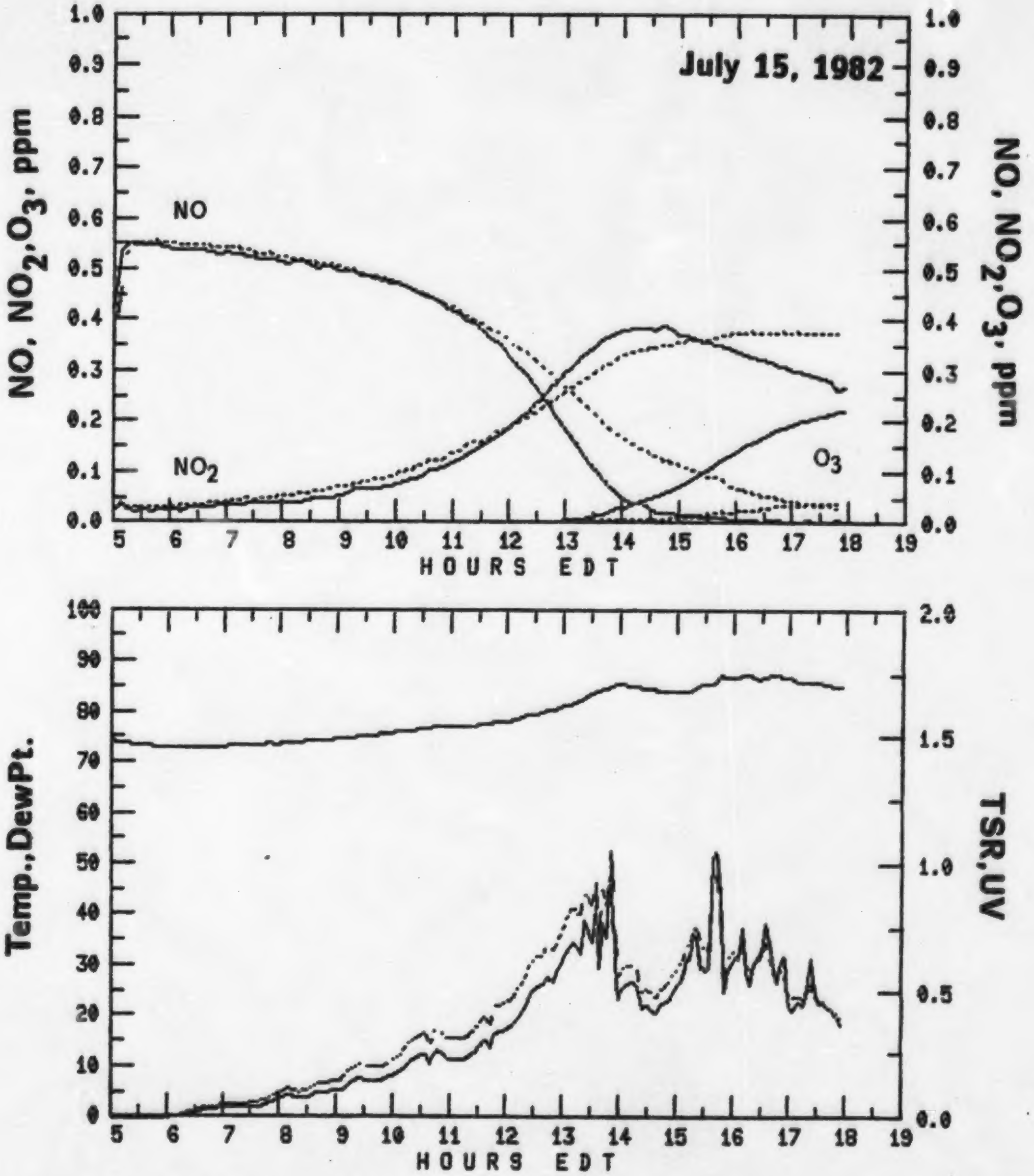


Figure D6. TOP: Plymouth Volare, direct injection + toluene, NMHC= 1.88 + 0.43 ppmC, (dashed lines); Plymouth Volare, direct injection + m-xylene, NMHC= 1.71 + 0.53 ppmC, (solid lines). BOTTOM: Chamber air temperature and dew point; ambient total solar and ultraviolet radiation;

July 20, 1982

Different Conditions from Direct Injection (RED) and Cryocondensor Sample (BLUE) from 1972 Dodge Charger

INITIAL CONDITIONS:	BLUE	RED
NO	0.021	0.045
NO2	0.040	0.016
DIRECT CHARGER	0.0	1.05
CRYO CHARGER	1.95	0.0

	MORN	AFTERNOON
SUNLIGHT AND WEATHER:	6.0/10.0	4.0/10.0
TEMPERATURE F:	72.0	97.0

INSTRUMENTS USED:

1: CARLE I GC
2: CARLE II GC
3: PERKIN ELMER 900 GC
4: BECKMAN 6800 THC/CH4
5: CEA FORMALDEHYDE
6: VARIAN GC

DATA EXCEPTIONS:

1: DNPH ALDEHYDES;

CHAMBER CONDITIONS:

1: 6 HOURS VENTING BEFORE RUN.
2: DRYING PERFORMED; NO CONDENSATION OBSERVED.

SPECIAL PROBLEMS OR CONCERNS:

1: POOR SUNLIGHT.
2: INITIAL NMHC NOT MATCHED. VERY LOW INITIAL NOX .
3: EXPERIMENT NOT TO BE PROCESSED.

EXPERIMENT STARTS:	0600
INITIAL CONDITIONS ESTABLISHED:	0530
EXPERIMENTS ENDS:	1800

RUN QUALITY INDEX:	4/10

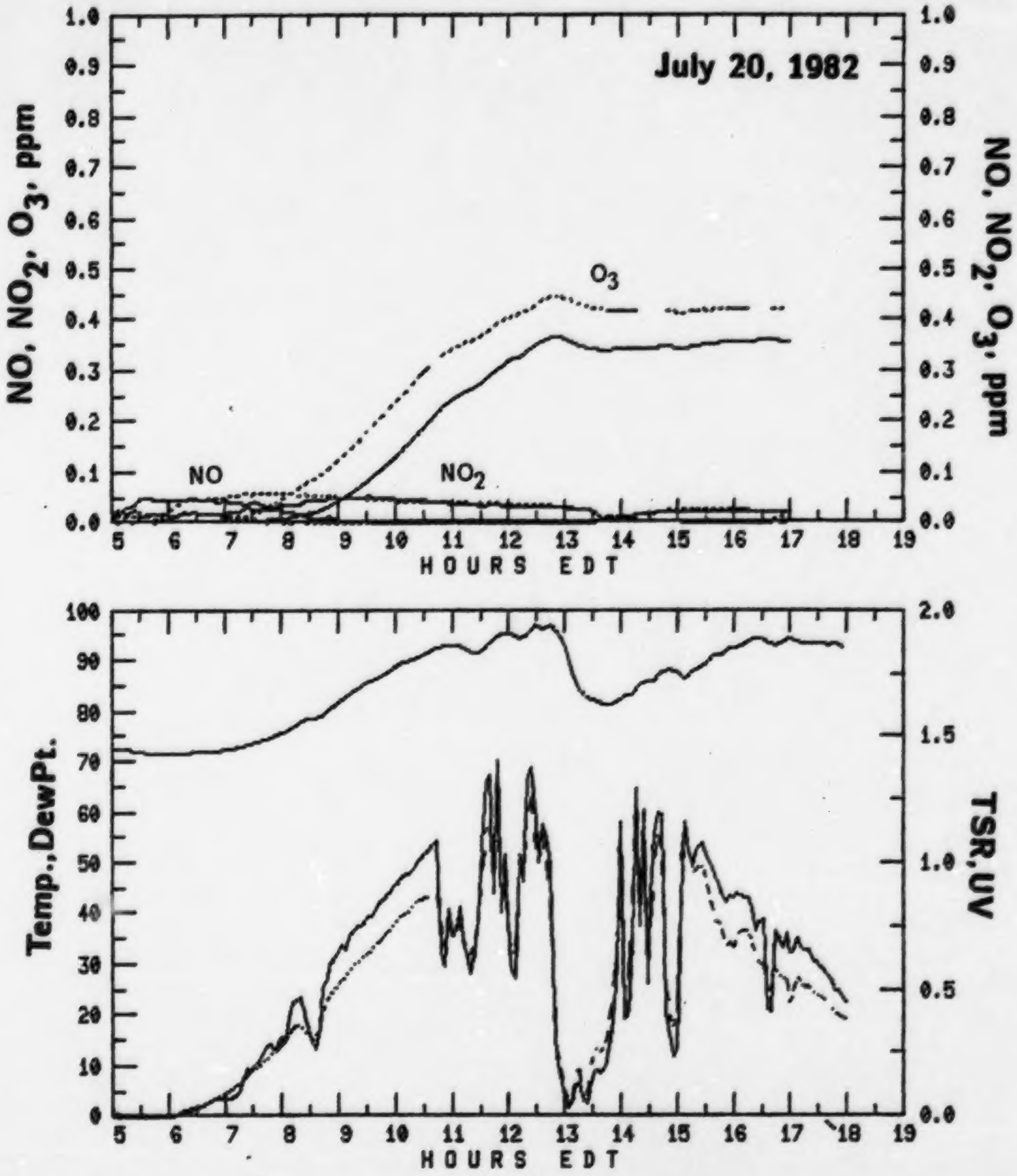


Figure D7. TOP: Dodge Charger, cryocondensor injection , NMHC= 1.95 ppmC, (dashed lines); Dodge Charger, direct injection, NMHC= 1.05 ppmC, (solid lines).
BOTTOM: Chamber air temperature and dew point; ambient total solar and ultraviolet radiation;

August 3, 1982

EKMA Test : Two Levels of Initial Conditions from 1972 Dodge Charger

INITIAL CONDITIONS:	BLUE	RED
NO	0.099	0.413
NO2	0.066	0.043
NMHC	1.251	2.451
CO	10.586	18.377

	MORN	AFTERNOON
SUNLIGHT AND WEATHER:	7.25/10.0	6.58/10.0
TEMPERATURE F:	69.0	93.0

INSTRUMENTS USED:

1: CARLE I GC
2: CARLE II GC
3: PERKIN ELMER 900 GC
4: BECKMAN 6800 THC/CH4
5: CEA FORMALDEHYDE
6: VARIAN GC

DATA EXCEPTIONS:

1: DNPH ALDEHYDE DATA EXISTS FOR THIS DAY, BUT FORMALDEHYDE WAS THE ONLY MAJOR DNPH ALDEHYDE OBSERVED IN THE CHROMATOGRAM THEREFORE ONLY CEA 555 COLORIMETRIC HCHO (REGULAR) DATA REPORTED.

2: PROBLEMS WITH PE900 FOR LOW CONCENTRATION AROMATIC DATA.

CHAMBER CONDITIONS:

1: DRYING WAS PERFORMED
2: CONDENSATION WAS OBSERVED ON BOTH SIDES

SPECIAL PROBLEMS OR CONCERNS: NONE

EXPERIMENT STARTS:	0628
INITIAL CONDITIONS ESTABLISHED:	0535
EXPERIMENTS ENDS:	1655

RUN QUALITY INDEX:	8.7/10.0

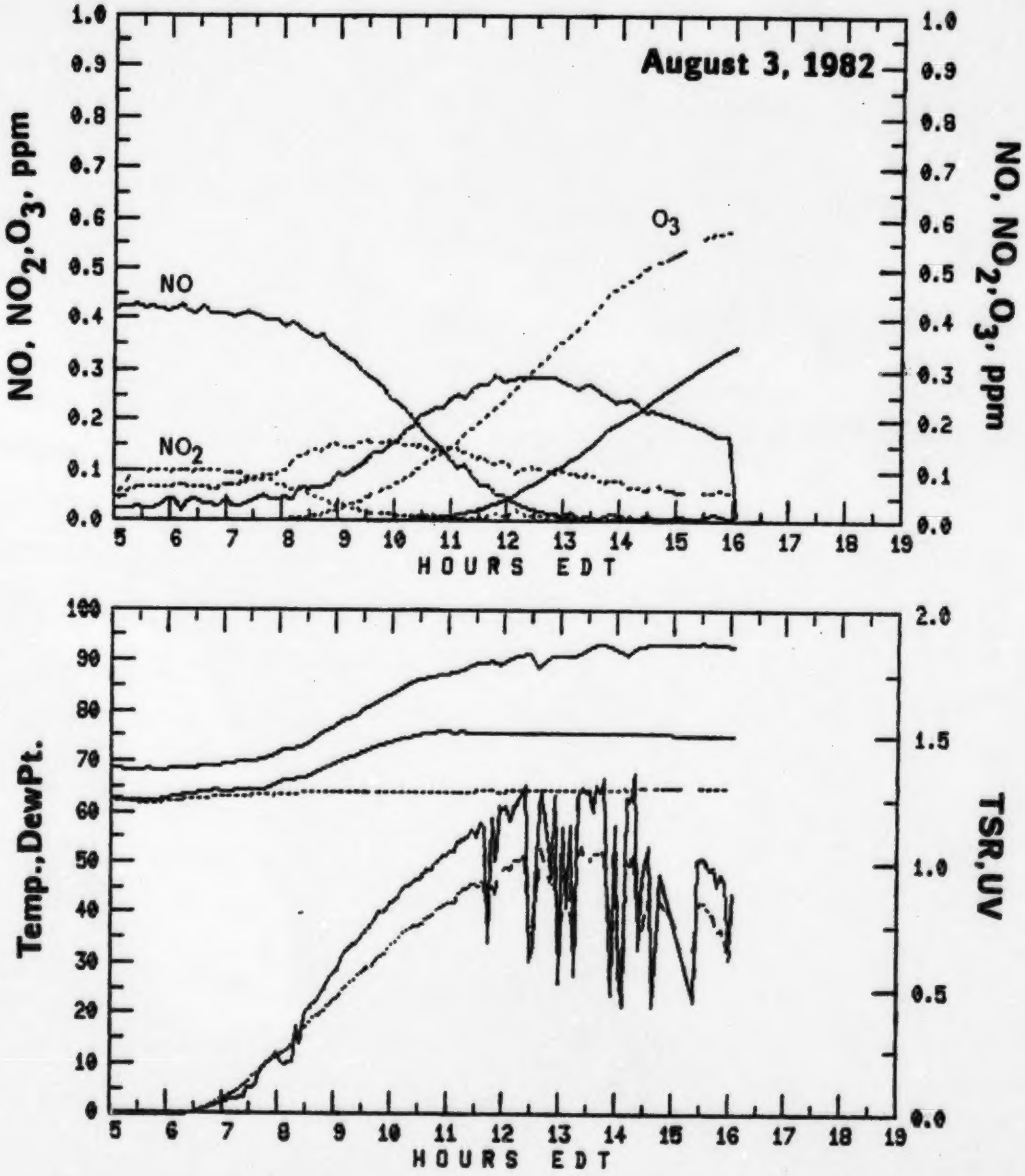


Figure D8. TOP: Dodge Charger, cryocondensor injection , NMHC= 1.25 ppmC, (solid lines); Dodge Charger, direct injection, NMHC= 2.45 ppmC, (dashed lines).
BOTTOM: Chamber air temperature and dew point; ambient total solar and ultraviolet radiation;

Initial Conditions for August 3, 1982

			DC/76/Dir			DC/76/Dir		
			BLUE			RED		
	Cnum	Split *	PPMC	%C	PPMV	RED	%C	PPMV
PARAFFINS								
ethane	2		0.016	1.28	0.008	0.032	1.31	0.016
propane	3		ND	NA	ND	ND	NA	ND
n-butane	4		NM	NA	NM	NM	NA	NM
i-butane	4		NM	NA	NM	NM	NA	NM
i-pentane	5		T	NA	T	T	NA	T
n-pentane	5		ND	NA	ND	ND	NA	ND
2-me-pentane	6		ND	NA	ND	ND	NA	ND
trime-pentanes	8		NM	NA	NM	NM	NA	NM
octane	8		NM	NA	NM	NM	NA	NM
C6 unk(C1G)	6		ND	NA	ND	ND	NA	ND
Sub-total			0.016	1.28	0.008	0.032	1.31	0.016
OLEFINS								
ethylene	2		0.228	18.23	0.114	0.307	12.53	0.154
propylene	3		0.062	4.96	0.021	0.090	3.67	0.030
1-butene	4		NM	NA	NM	NM	NA	NM
c-2-butene	4		NM	NA	NM	NM	NA	NM
t-2-butene	4		NM	NA	NM	NM	NA	NM
1,3butadiene	4		NM	NA	NM	NM	NA	NM
2-me-1-butene	5		ND	NA	ND	ND	NA	ND
2-me-2-butene	5		ND	NA	ND	ND	NA	ND
Sub-total			0.290	23.18	0.135	0.397	16.20	0.184

AROMATICS								
benzene	6		0.109	8.71	0.018	0.140	5.71	0.023
toluene	7		0.081	6.47	0.012	0.097	3.96	0.014
mp-xylene	8		0.021	1.68	0.003	0.039	1.59	0.005
et-benzenes	8		ND	NA	ND	ND	NA	ND
pro-benzenes	9		ND	NA	ND	ND	NA	ND
o-xylene	8		ND	NA	ND	ND	NA	ND
135-C3-benzene	9		ND	NA	ND	ND	NA	ND
123-C3-benzene	9		ND	NA	ND	ND	NA	ND
124-C3-benzene	9		ND	NA	ND	ND	NA	ND
dimeet-benzene	10		ND	NA	ND	ND	NA	ND
m-eth-toluene	9		ND	NA	ND	ND	NA	ND
o-eth-toluene	9		ND	NA	ND	ND	NA	ND
styrene	8		ND	NA	ND	ND	NA	ND
napthalene	10		ND	NA	ND	ND	NA	ND
2me-napthalene	11		ND	NA	ND	ND	NA	ND
1me-mapthalene	11		ND	NA	ND	ND	NA	ND
others	10	4	ND	NA	ND	ND	NA	ND
Sub-total			0.211	16.87	0.032	0.276	11.26	0.042
ACETYLENE								
acetylene	2		0.206	16.47	0.103	0.310	12.65	0.155
TOTAL MEASURED SPECIES			0.723	57.79	0.278	1.015	41.41	0.397
Unspeciated Carbon			0.528	42.21		1.436	58.59	
FINAL NMHC			1.251			2.451		

```
                                                     |
                                                     |

#####################################################|##########################
                                                     |
SUMMARY                                              |
                       PPMC       %C      Car Num |  PPMC       %C      Car Num
                                                     |
    Meas PAR            0.016      1.28      2.00 |   0.032      1.31      2.00
    Est  PAR            0.230     18.39      5.78 |   0.500     20.40      5.73
                    ---------------------------|---------------------------
    TOT  PAR       5    0.246     19.66      5.15 |   0.532     21.71      5.15
                                                     |
                                                     |
    Meas OLE            0.290     23.18      2.15 |   0.397     16.20      2.16
     Est OLE            0.000      0.00      0.00 |   0.120      9.59      6.24
                    ---------------------------|---------------------------
     TOT OLE       5    0.290     23.18      2.55 |   0.517     21.09      2.55
                                                     |
                                                     |
    Meas ARO            0.211     16.87      6.52 |   0.276     11.26      6.56
     Est ARO            0.290     23.18      9.22 |   0.600     47.96      8.63
                    ---------------------------|---------------------------
                   5    0.501     40.05      7.85 |   0.876     35.74      7.85
                                                     |
    Meas ACE            0.206     16.47      2.00 |   0.310     12.65      2.00
                    ---------------------------|---------------------------
     TOT ACE            0.206     16.47      2.00 |   0.310     12.65      2.00
                                                     |
--------------      ---------------------------|---------------------------
--------------      ---------------------------|---------------------------
     Spec HC            0.723     57.79           |   1.015     41.41
   Unspec HC            0.520     41.57           |   1.220     49.78
                    ------------------            |------------------
     TOT NMHC           1.243     99.36           |   2.235     91.19
```

August 5, 1982

Different Conditions from Direct Injection (RED) and Cryocondensor Sample (BLUE) from 1972 Dodge Charger

INITIAL CONDITIONS:	BLUE	RED
NO	0.32	0.32
NO2	0.06	0.06
DIRECT CHARGER	0.0	1.55
CRYO CHARGER	1.40	0.0
	MORN	AFTERNOON
SUNLIGHT AND WEATHER:	1.0/10.0	6.0/10.0
TEMPERATURE F:	73.5	93.0

INSTRUMENTS USED:
1: CARLE I GC
2: CARLE II GC
3: PERKIN ELMER 900 GC
4: BECKMAN 6800 THC/CH4
5: CEA FORMALDEHYDE
6: VARIAN GC

DATA EXCEPTIONS: NO DNPH ALDEHYDE DATA;

CHAMBER CONDITIONS:
1: MORE THAN 24 HOURS VENTING BEFORE RUN.
2: DRYING PERFORMED; NO CONDENSATION OBSERVED.

SPECIAL PROBLEMS OR CONCERNS:
1: VERY POOR MORNING SUN.
2: PROBLEMS WITH NOX MONITOR.
3: EXPERIMENT NOT TO BE PROCESSED.

EXPERIMENT STARTS: (SUNRISE)	0626
INITIAL CONDITIONS ESTABLISHED:	0638
EXPERIMENTS ENDS:	1640

RUN QUALITY INDEX: 3/10.0

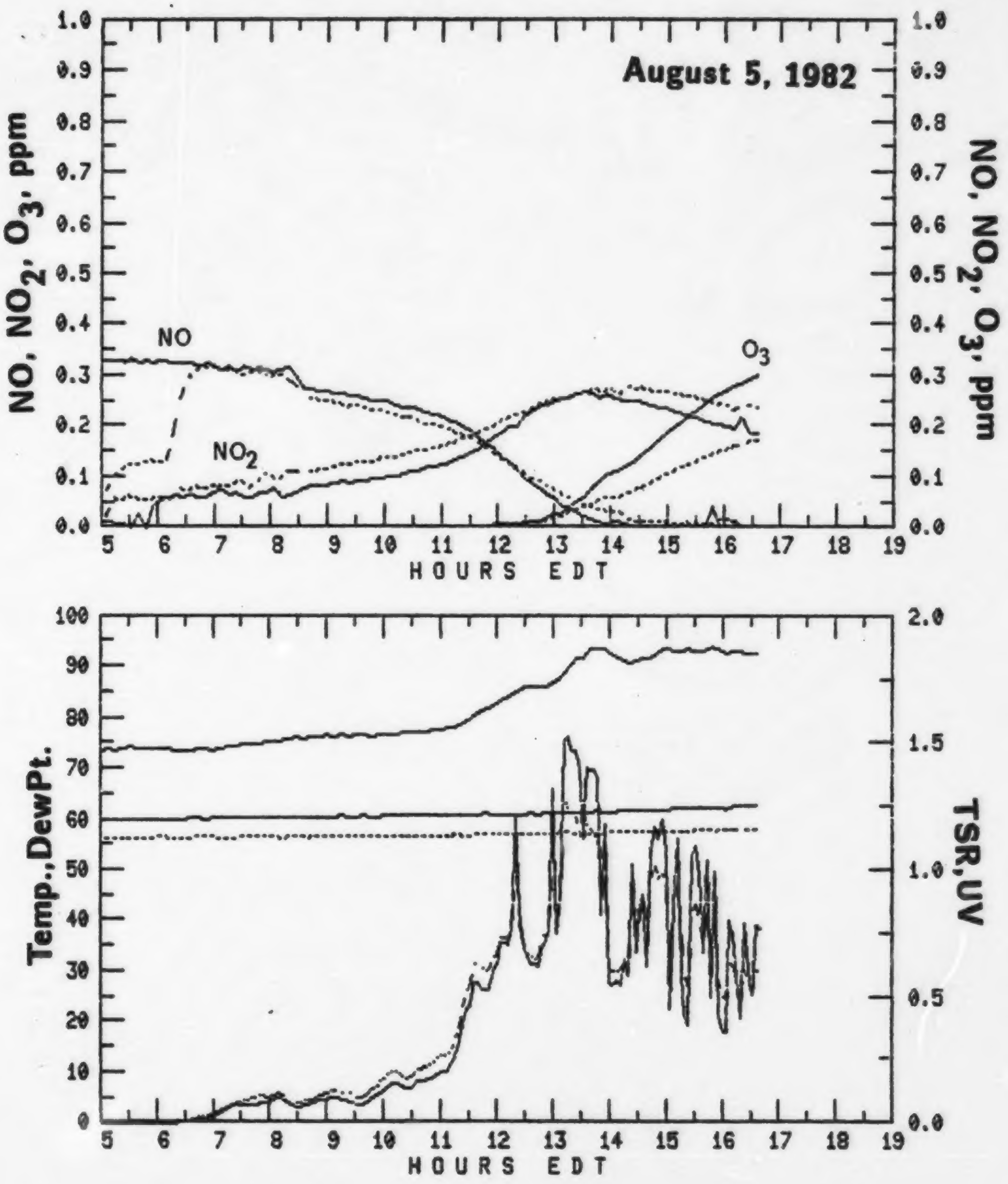


Figure D9. TOP: Dodge Charger, cryocondensor injection , NMHC= 1.45 ppmC, (dashed lines); Dodge Charger, direct injection, NMHC= 1.55 ppmC, (solid lines).
BOTTOM: Chamber air temperature and dew point; ambient total solar and ultraviolet radiation;

August 6, 1982

Different Conditions from Direct Injection (RED) and Cryocondensor Sample (BLUE) from 1972 Dodge Charger

INITIAL CONDITIONS:	BLUE	RED
NMHC	1.066	1.382
NO	0.259	0.342
NO2	0.099	0.032

	MORN	AFTERNOON
SUNLIGHT AND WEATHER:	8.25/10.0	9.0/10.0
TEMPERATURE F:	71.0	96.0

INSTRUMENTS USED:

1: CARLE I GC
2: CARLE II GC
3: PERKIN ELMER 900 GC
4: BECKMAN 6800 THC/CH4
5: CEA FORMALDEHYDE
6: VARIAN GC

DATA EXCEPTIONS:

1: NO DNPH ALDEHYDE DATA;
2: LOW CONCENTRATION OF NMHC PREVENTED MORE DETAILED HC SPECIATION.

CHAMBER CONDITIONS:

1: MORE THAN 7 HOURS VENTING BEFORE RUN.
2: DRYING PERFORMED; NO CONDENSATION OBSERVED.

SPECIAL PROBLEMS OR CONCERNS: NONE

EXPERIMENT STARTS: 0612
INITIAL CONDITIONS ESTABLISHED: 0600
EXPERIMENTS ENDS: 1529

RUN QUALITY INDEX: 7.7/10.0

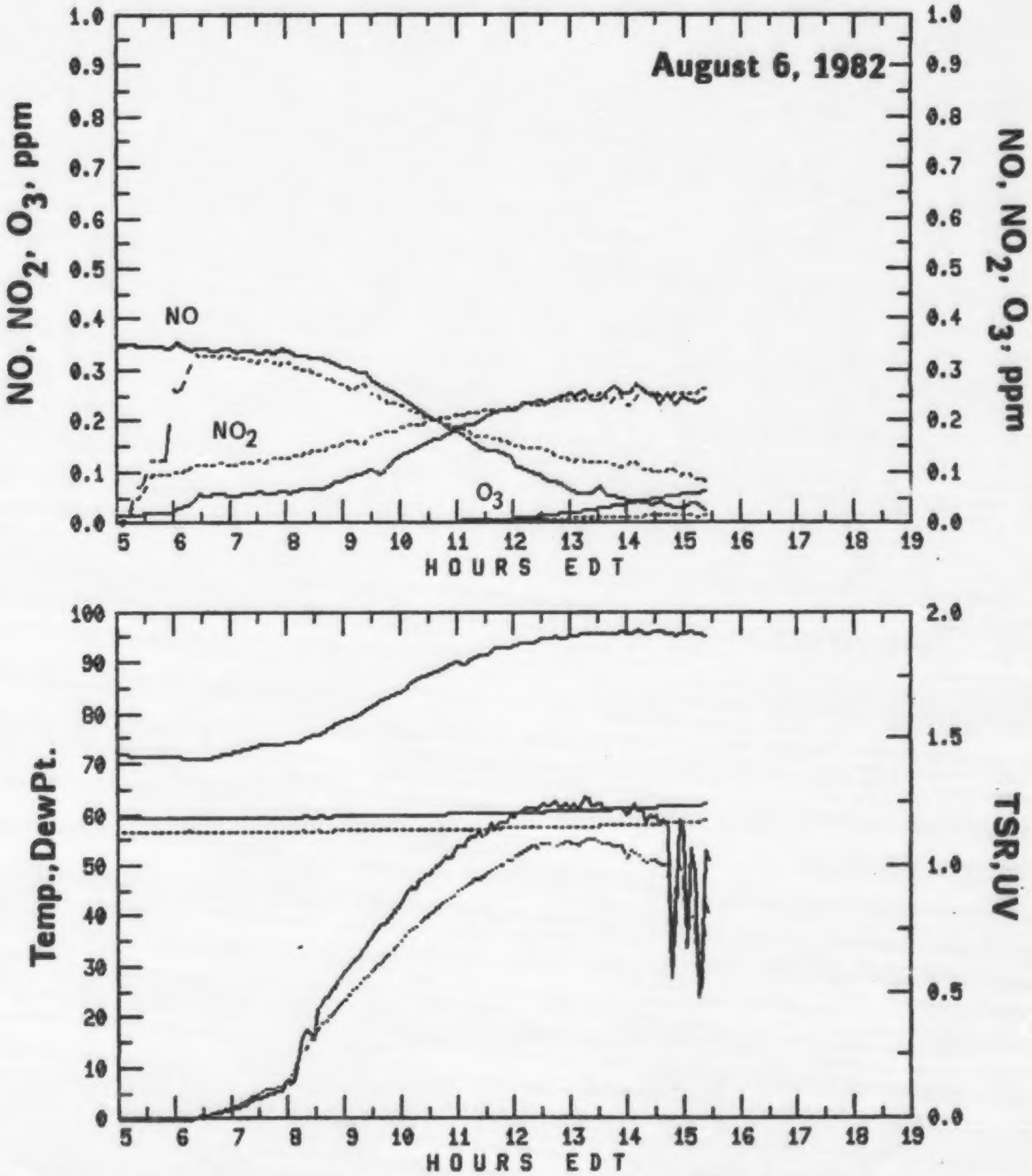


Figure D10. TOP: Dodge Charger, cryocondensor injection , NMHC= 1.07 ppmC, (dashed lines); Dodge Charger, direct injection, NMHC= 1.38 ppmC, (solid lines).
BOTTOM: Chamber air temperature and dew point; ambient total solar and ultraviolet radiation;

August 7, 1982

Matched Conditions from Direct Injection (RED) and Cryocondensor Sample (BLUE) from 1972 Dodge Charger

INITIAL CONDITIONS:	BLUE	RED
NMHC	1.454	1.481
NO	0.243	0.247
NO2	0.046	0.046

	MORN	AFTERNOON
SUNLIGHT AND WEATHER:	5.5/10.0	4.5/10.0
TEMPERATURE F:	71.0	98.0

INSTRUMENTS USED:
1: CARLE I GC
2: BECKMAN 6800 THC/CH4
3: CEA FORMALDEHYDE
4: VARIAN GC

DATA EXCEPTIONS: LOW NMHC AND OTHER INSTRUMENT PROBLEMS RESULTED IN LOSS OF MOST HC DATA.

CHAMBER CONDITIONS:
1: 6 HOURS VENTING BEFORE RUN.
2: DRYING PERFORMED; CONDENSATION OBSERVED IN RED SIDE.

SPECIAL PROBLEMS OR CONCERNS:
1: PROBLEMS WITH NOX INSTRUMENT.
2: CONDENSATION IN RED SIDE.
3: LACK OF HC DATA IN MORNING. LOW CONCENTRATION NMHC.

EXPERIMENT STARTS:	0620
INITIAL CONDITIONS ESTABLISHED:	0600
EXPERIMENTS ENDS:	1636

RUN QUALITY INDEX:	7.64/10.0

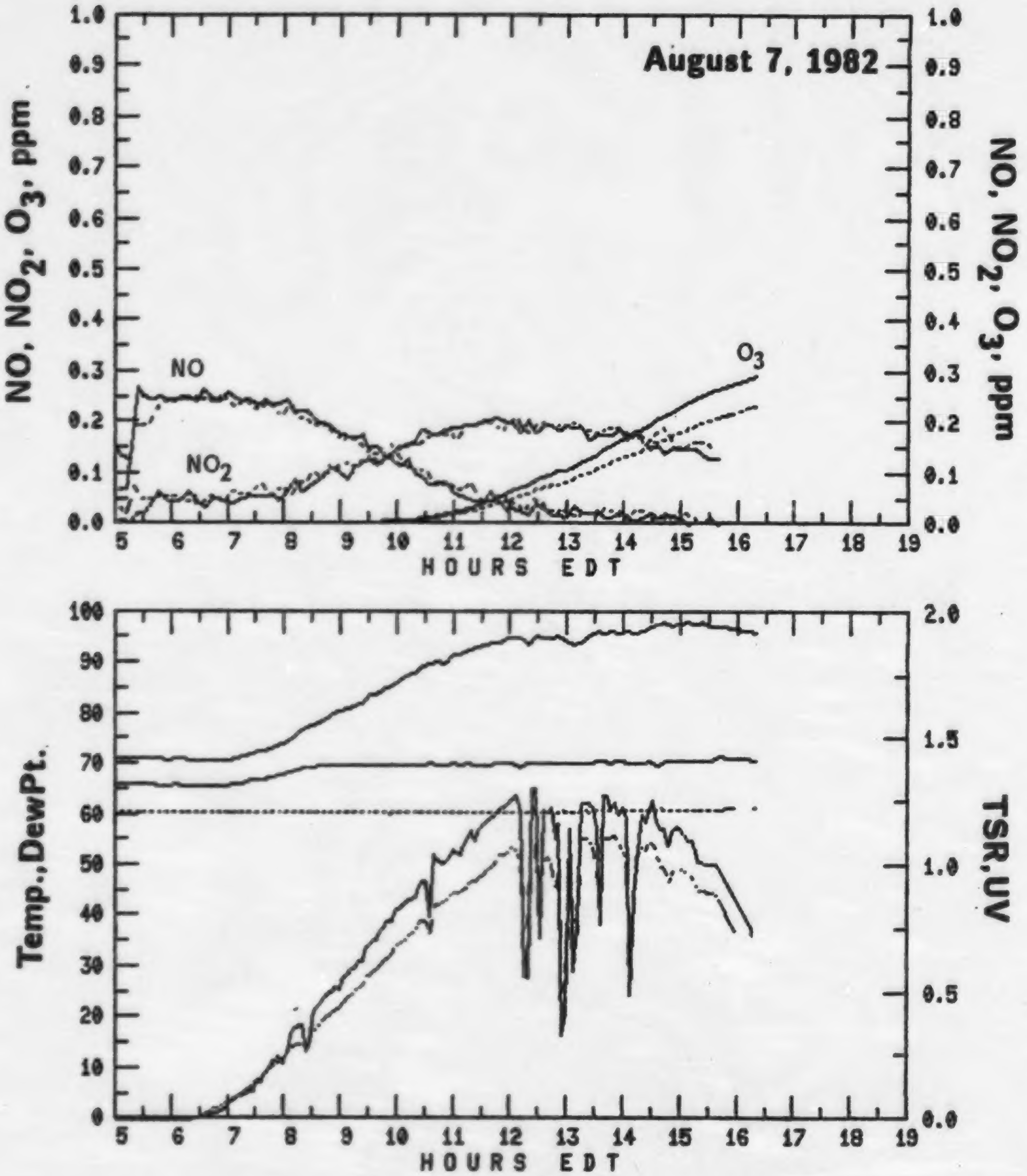


Figure D11. TOP: Dodge Charger, cryocondensor injection , NMHC= 1.45 ppmC, (dashed lines); Dodge Charger, direct injection, NMHC= 1.48 ppmC, (solid lines).
BOTTOM: Chamber air temperature and dew point; ambient total solar and ultraviolet radiation;

August 11, 1982

Different Conditions from Direct Injection (RED) and Cryocondensor Sample (BLUE) from 1972 Dodge Charger

INITIAL CONDITIONS:	BLUE	RED
NO	0.35	0.35
NO2	0.13	0.12
DIRECT CHARGER	0.0	1.53
CRYO CHARGER	1.05	0.0

	MORN	AFTERNOON
SUNLIGHT AND WEATHER:	2.0/10.0	2.0/10.0
TEMPERATURE F:	74.0	89.0

INSTRUMENTS USED:

1: CARLE I GC

2: CARLE II GC

3: PERKIN ELMER 900 GC

4: BECKMAN 6800 THC/CH4

5: CEA FORMALDEHYDE

6: VARIAN GC

DATA EXCEPTIONS: NO DNPH ALDEHYDE DATA;

CHAMBER CONDITIONS:

1: MORE THAN 24 HOURS VENTING BEFORE RUN.

2: DRYING PERFORMED; NO CONDENSATION OBSERVED.

SPECIAL PROBLEMS OR CONCERNS:

1: VERY POOR SUN.

2: PROBLEMS WITH NOX MONITOR.

3: EXPERIMENT NOT TO BE PROCESSED.

EXPERIMENT STARTS: (SUNRISE)	0625
INITIAL CONDITIONS ESTABLISHED:	0600
EXPERIMENTS ENDS:	1800

RUN QUALITY INDEX:	2/10.0

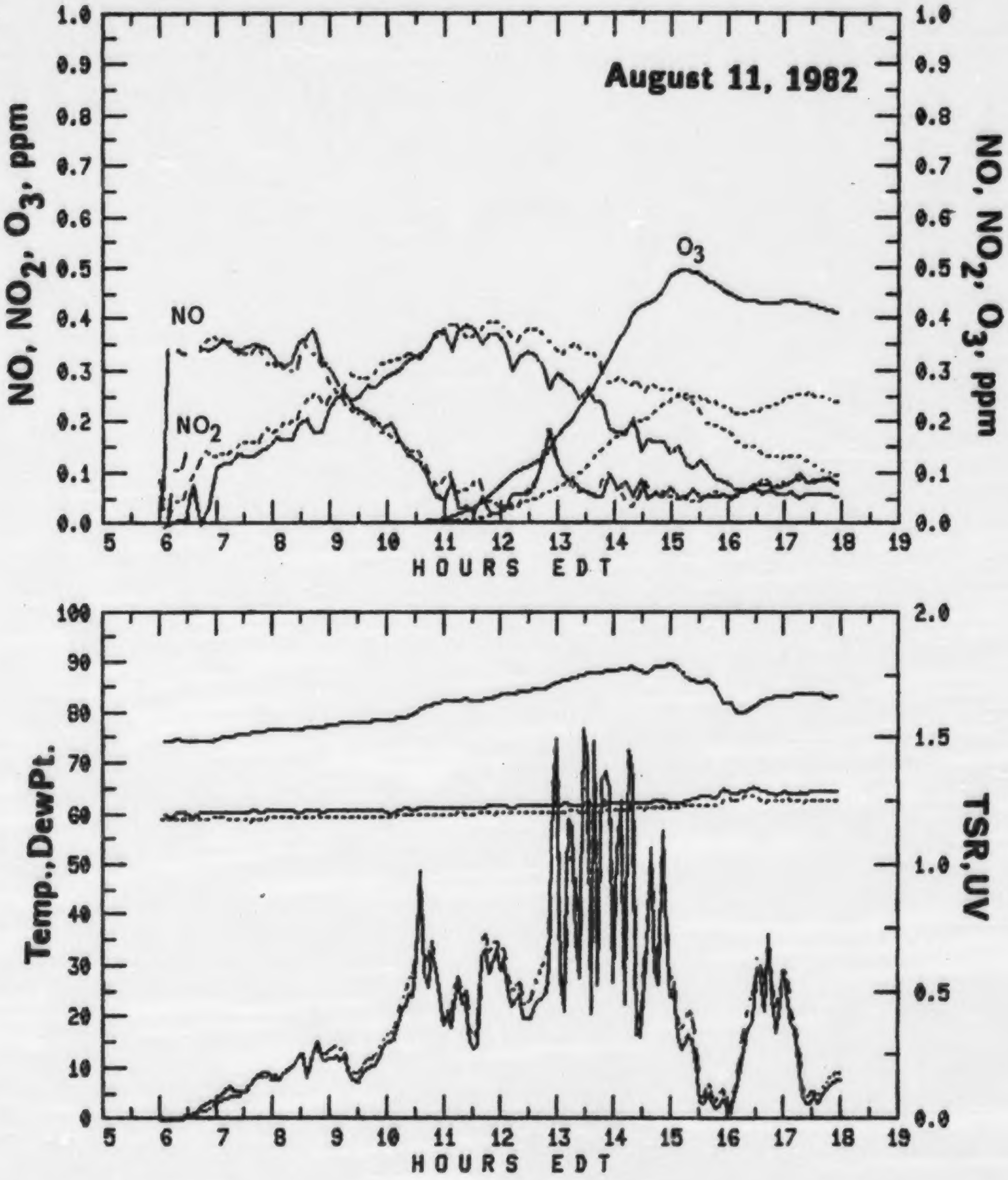


Figure D12 TOP: Dodge Charger, cryocondensor injection , NMHC= 1.05 ppmC, (dashed lines); Dodge Charger, direct injection, NMHC= 1.53 ppmC, (solid lines).
BOTTOM: Chamber air temperature and dew point; ambient total solar and ultraviolet radiation;

September 17, 1982

Matched Conditions from Direct Injection (RED) and Cryocondensor Sample (BLUE) from 1972 Dodge Charger

INITIAL CONDITIONS:	BLUE	RED
NO	0.159	0.158
NO2	0.095	0.097
NMHC	2.419	2.160
CO	24.939	22.321

	MORN	AFTERNOON
SUNLIGHT AND WEATHER:	6.0/10.0	6.5/10.0
TEMPERATURE F:	67.0	87.0

INSTRUMENTS USED:

1: CARLE I GC

2: CARLE II GC

3: PERKIN ELMER 900 GC

4: BECKMAN 6800 THC/CH4

5: CEA FORMALDEHYDE

6: VARIAN GC

DATA EXCEPTIONS: NONE

CHAMBER CONDITIONS:

1: 6 HOURS OF VENTING

2: DRYING WAS PERFORMED

3: SOME CONDENSATION WAS OBSERVED IN RED SIDE.

SPECIAL PROBLEMS OR CONCERNS:

1: DEWPOINT WAS SOMEWHAT GREATER IN RED SIDE.

EXPERIMENT STARTS:	0700
INITIAL CONDITIONS ESTABLISHED:	0557
EXPERIMENTS ENDS:	1800

RUN QUALITY INDEX: 8.5/10.0

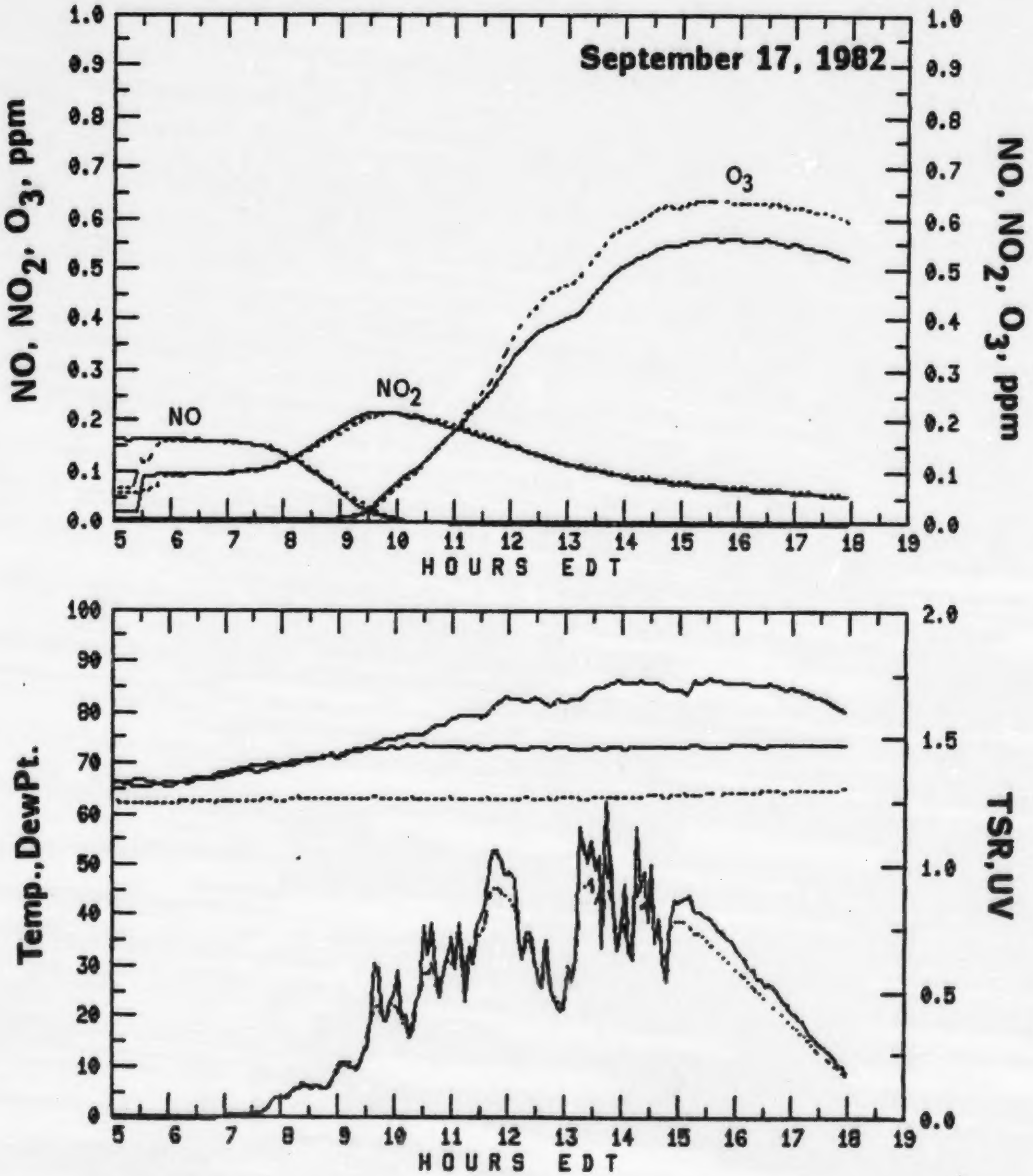


Figure D13. TOP: Dodge Charger, cryocondensor injection , NMHC= 2.42 ppmC, (dashed lines); Dodge Charger, direct injection, NMHC= 2.16 ppmC, (solid lines).
BOTTOM: Chamber air temperature and dew point; ambient total solar and ultraviolet radiation;

Initial Conditions for September 17,1982

			DC/66/Cryo			DC/66/Dir		
			BLUE			RED		
	Cnum	Split *	PPMC	%C	PPMV	RED	%C	PPMV
PARAFFINS								
ethane	2		0.057	2.36	0.029	0.048	2.22	0.024
propane	3		0.036	1.49	0.012	0.029	1.34	0.010
n-butane	4		0.152	6.28	0.038	0.157	7.27	0.039
i-butane	4		NM	NA	NM	NM	NA	NM
i-pentane	5		0.030	1.24	0.006	0.030	1.39	0.006
n-pentane	5		ND	NA	ND	ND	NA	ND
2-me-pentane	6		ND	NA	ND	ND	NA	ND
trime-pentanes	8		NM	NA	NM	NM	NA	NM
octane	8		NM	NA	NM	NM	NA	NM
C6 unk(C1G)	6		ND	NA	ND	ND	NA	ND
Sub-total			0.275	11.37	0.085	0.264	12.22	0.079
OLEFINS								
ethylene	2		0.260	10.75	0.130	0.227	10.51	0.114
propylene	3		0.148	6.12	0.049	0.134	6.20	0.045
1-butene	4		NM	NA	NM	NM	NA	NM
c-2-butene	4		NM	NA	NM	NM	NA	NM
t-2-butene	4		NM	NA	NM	NM	NA	NM
1,3butadiene	4		NM	NA	NM	NM	NA	NM
2-me-1-butene	5		ND	NA	ND	ND	NA	ND
2-me-2-butene	5		ND	NA	ND	ND	NA	ND
Sub-total			0.408	16.87	0.179	0.361	16.71	0.158

AROMATICS								
benzene	6		0.268	11.08	0.045	0.239	11.06	0.040
toluene	7		0.192	7.94	0.027	0.180	8.33	0.026
mp-xylene	8		0.065	2.69	0.008	0.071	3.29	0.009
et-benzenes	8		0.021	0.87	0.003	0.022	1.02	0.003
pro-benzenes	9		ND	NA	ND	ND	NA	ND
o-xylene	8		0.028	1.16	0.004	0.029	1.34	0.004
135-C3-benzene	9		0.009	0.37	0.001	0.009	0.42	0.001
123-C3-benzene	9		0.008	0.33	0.001	0.005	0.23	0.001
124-C3-benzene	9		0.031	1.28	0.003	0.035	1.62	0.004
dimeet-benzene	10		0.016	0.66	0.002	0.028	1.30	0.003
m-eth-toluene	9		0.028	1.16	0.003	0.034	1.57	0.004
o-eth-toluene	9		0.020	0.83	0.002	0.020	0.93	0.002
styrene	8		0.018	0.74	0.002	0.022	1.02	0.003
napthalene	10		0.037	1.53	0.004	0.033	1.53	0.003
2me-napthalene	11		ND	NA	ND	ND	NA	ND
1me-mapthalene	11		ND	NA	ND	ND	NA	ND
others	10	4	0.053	2.19	0.005	0.063	2.92	0.006
Sub-total			0.794	32.82	0.110	0.790	36.57	0.107
ACETYLENE								
acetylene	2		0.536	22.16	0.268	0.469	21.71	0.235
TOTAL MEASURED SPECIES			2.013	83.22	0.642	1.884	87.22	0.579
Unspeciated Carbon			0.406	16.78		0.276	12.78	
FINAL NMHC			2.419			2.160		

```
                                                          |
                                                          |
##########################################################|############################
                                                          |
SUMMARY                                                   |
                                PPMC       %C    Car Num  |  PPMC       %C     Car Num
                                                          |
     Meas PAR                  0.275     11.37     3.25   |  0.264     12.22     3.35
     Est  PAR                  0.350     14.47     9.50   |  0.276     12.78    10.64
                            ------------------------------|----------------------------
     TOT  PAR              5   0.625     25.84     5.15   |  0.540     25.00     5.15
                                                          |
                                                          |
     Meas OLE                  0.408     16.87     2.28   |  0.361     16.71     2.28
      Est OLE                  0.000      0.00     0.00   |  0.000      0.00     0.00
                            ------------------------------|----------------------------
      TOT OLE              5   0.408     16.87     2.55   |  0.361     16.71     2.55
                                                          |
                                                          |
     Meas ARO                  0.794     32.82     7.23   |  0.790     36.57     7.36
      Est ARO                  0.000      0.00     0.00   |  0.000      0.00     0.00
                            ------------------------------|----------------------------
                           5   0.794     32.82     7.85   |  0.790     36.57     7.85
                                                          |
     Meas ACE                  0.536     22.16     2.00   |  0.469     21.71     2.00
                            ------------------------------|----------------------------
      TOT ACE                  0.536     22.16     2.00   |  0.469     21.71     2.00
                                                          |
--------------              ------------------------------|----------------------------
--------------              ------------------------------|----------------------------
      Spec HC                  2.013     83.22            |  1.884     87.22
    Unspec HC                  0.350     14.47            |  0.276     12.78
                            ------------------            |------------------
     TOT NMHC                  2.363     97.68            |  2.160    100.00
```

September 29, 1982

Matched Direct Injections from 1972 Dodge Charger (RED) and 1979 Plymouth Volare (BLUE)

INITIAL CONDITIONS:	BLUE	RED
NO	0.316	0.317
NO2	0.074	0.075
NMHC	1.740	1.723
CO	20.596	16.224

	MORN	AFTERNOON
SUNLIGHT AND WEATHER:	7.0/10.0	3.0/10.0
TEMPERATURE F:	56.0	83.0

INSTRUMENTS USED:

1: CARLE I GC
2: CARLE II GC
3: DNPH ALDEHYDES (QUALITATIVE)
4: BECKMAN 6800 THC/CH4
5: CEA FORMALDEHYDE
6: VARIAN GC

DATA EXCEPTIONS: NO PE900 AROMATIC DATA - AROMATIC CONTRIBUTION TO NMHC ESTIMATED FROM TOLUENE AND BENZENE MEASUREMENTS AND COMPOSITION DATA FROM OTHER EXPERIMENTS WITH THESE TEST VEHICLES.

CHAMBER CONDITIONS:

1: 8 HOURS OF VENTING
2: DRYING WAS PERFORMED
3: CONDENSATION WAS OBSERVED

SPECIAL PROBLEMS OR CONCERNS:

1: ESTIMATED INITIAL NMHC CONCENTRATION.

EXPERIMENT STARTS:	0700
INITIAL CONDITIONS ESTABLISHED:	0600
EXPERIMENTS ENDS:	1647
RUN QUALITY INDEX:	8.4/10.0

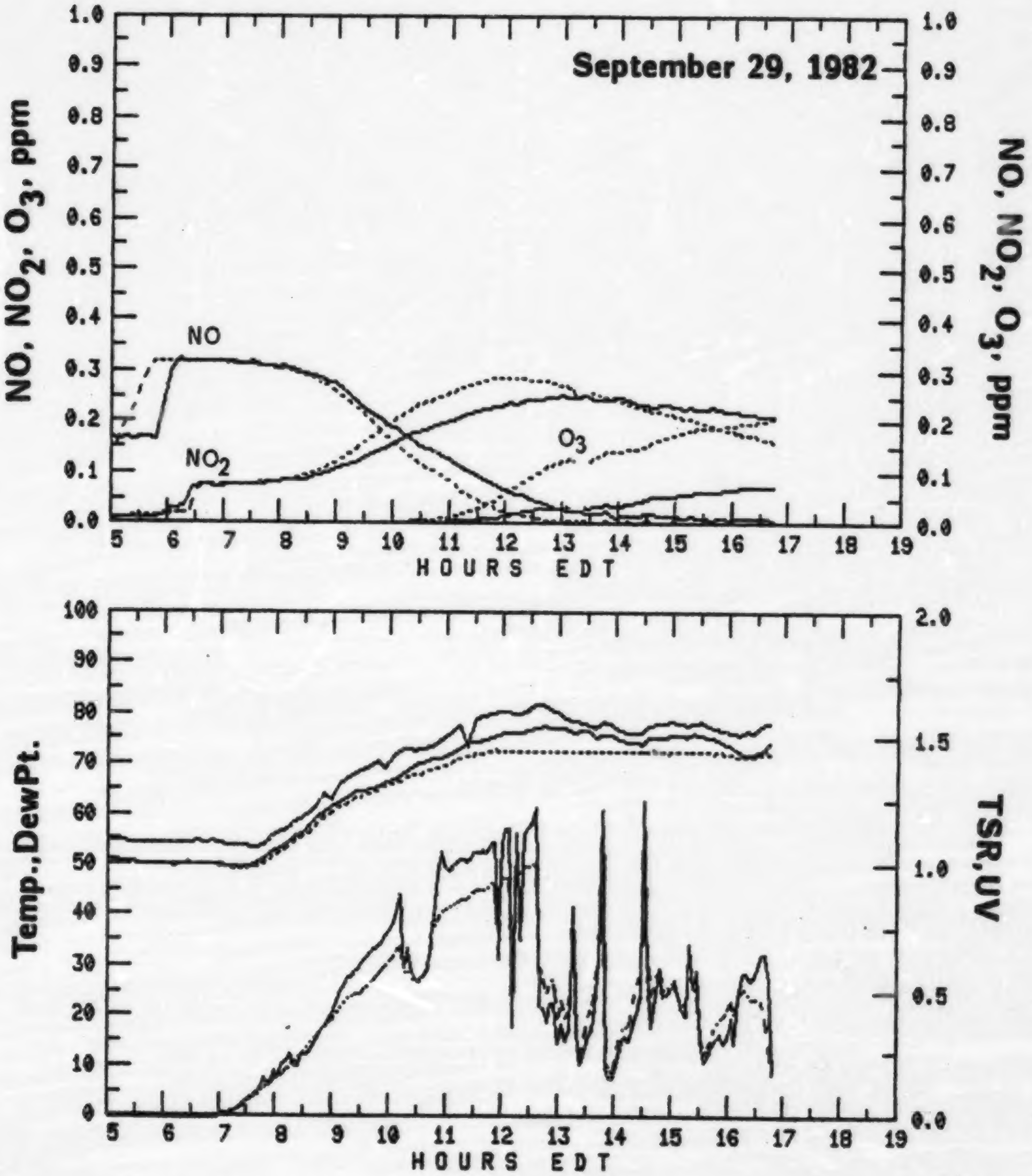


Figure D14. TOP: Plymouth Volare, direct injection , NMHC= 1.74 ppmC, (dashed lines); Dodge Charger, direct injection, NMHC= 1.72 ppmC, (solid lines).
BOTTOM: Chamber air temperature and dew point; ambient total solar and ultraviolet radiation;

Initial Conditions for September 29,1982

			PV/66			DC/66		
			BLUE			RED		
	Cnum	Split *	PPMC	%C	PPMV	RED	%C	PPMV
PARAFFINS								
ethane	2		0.026	1.49	0.013	0.021	1.22	0.011
propane	3		ND	NA	ND	ND	NA	ND
n-butane	4		0.058	3.33	0.015	0.077	4.47	0.019
i-butane	4		ND	NA	ND	ND	NA	ND
i-pentane	5		T	NA	T	T	NA	T
n-pentane	5		ND	NA	ND	ND	NA	ND
2-me-pentane	6		T	NA	T	T	NA	T
trime-pentanes	8		NM	NA	NM	NM	NA	NM
octane	8		NM	NA	NM	NM	NA	NM
C6 unk(C1G)	6		ND	NA	ND	ND	NA	ND
Sub-total			0.084	4.83	0.028	0.098	5.69	0.030
OLEFINS								
ethylene	2		0.156	8.97	0.078	0.162	9.40	0.081
propylene	3		0.095	5.46	0.032	0.090	5.22	0.030
1-butene	4		NM	NA	NM	NM	NA	NM
c-2-butene	4		NM	NA	NM	NM	NA	NM
t-2-butene	4		NM	NA	NM	NM	NA	NM
1,3butadiene	4		NM	NA	NM	NM	NA	NM
2-me-1-butene	5		ND	NA	ND	ND	NA	ND
2-me-2-butene	5		T	NA	T	T	NA	T
Sub-total			0.251	14.43	0.110	0.252	14.63	0.111

AROMATICS								
benzene	6		0.122	7.01	0.020	0.088	5.11	0.015
toluene	7		0.214	12.30	0.031	0.181	10.50	0.026
mp-xylene	8		ND	NA	ND	ND	NA	ND
et-benzenes	8		ND	NA	ND	ND	NA	ND
pro-benzenes	9		ND	NA	ND	ND	NA	ND
o-xylene	8		ND	NA	ND	ND	NA	ND
135-C3-benzene	9		ND	NA	ND	ND	NA	ND
123-C3-benzene	9		ND	NA	ND	ND	NA	ND
124-C3-benzene	9		ND	NA	ND	ND	NA	ND
dimeet-benzene	10		ND	NA	ND	ND	NA	ND
m-eth-toluene	9		ND	NA	ND	ND	NA	ND
o-eth-toluene	9		ND	NA	ND	ND	NA	ND
styrene	8		ND	NA	ND	ND	NA	ND
napthalene	10		ND	NA	ND	ND	NA	ND
2me-napthalene	11		ND	NA	ND	ND	NA	ND
1me-napthalene	11		ND	NA	ND	ND	NA	ND
others	10	4	ND	NA	ND	ND	NA	ND
Sub-total			0.336	19.31	0.051	0.269	15.61	0.041
ACETYLENE								
acetylene	2		0.310	17.82	0.155	0.318	18.46	0.159
TOTAL MEASURED SPECIES			0.981	56.38	0.343	0.937	54.38	0.340
Unspeciated Carbon			0.759	43.62		0.786	45.62	
FINAL NMHC			1.740			1.723		

```
                                                                    |
                                                                    |
#####################################################|##########################
                                                                    |
SUMMARY                                                             |
                              PPMC        %C       Car Num |  PPMC        %C       Car Num
                                                                    |
     Meas PAR                0.084       4.83       3.05 |  0.098       5.69       3.29
     Est  PAR                0.300      17.24       6.37 |  0.300      17.41       6.31
                          ---------------------------|---------------------------
     TOT  PAR          5     0.384      22.07       5.15 |  0.398      23.10       5.15
                                                                    |
                                                                    |
     Meas OLE                0.251      14.43       2.29 |  0.252      14.63       2.27
      Est OLE                0.000       0.00       0.00 |  0.000       0.00       0.00
                          ---------------------------|---------------------------
      TOT OLE          5     0.251      14.43       2.55 |  0.252      14.63       2.55
                                                                    |
                                                                    |
     Meas ARO                0.336      19.31       6.60 |  0.269      15.61       6.64
      Est ARO                0.450      25.86       9.14 |  0.480      27.59       8.74
                          ---------------------------|---------------------------
                       5     0.786      45.17       7.85 |  0.749      43.47       7.85
                                                                    |
     Meas ACE                0.310      17.82       2.00 |  0.318      18.46       2.00
                          ---------------------------|---------------------------
      TOT ACE                0.310      17.82       2.00 |  0.318      18.46       2.00
                                                                    |
--------------            ---------------------------|---------------------------
--------------            ---------------------------|---------------------------
      Spec HC                0.981      56.38              |  0.937      54.38
    Unspec HC                0.750      43.10              |  0.780      45.27
                          -------------------              |-------------------
     TOT NMHC                1.731      99.48              |  1.717      99.65
```

October 6, 1982

Matched Direct Injections from 1972 Dodge Charger (BLUE) and 1979 Plymouth Volare (RED)

INITIAL CONDITIONS:	BLUE	RED
NO	0.369	0.371
NO2	0.097	0.099
NMHC	1.955	1.971
CO	24.654	20.686

	MORN	AFTERNOON
SUNLIGHT AND WEATHER:	9.0/10.0	8.0/10.0
TEMPERATURE F:	60.0	89.0

INSTRUMENTS USED:
1: CARLE I GC
2: CARLE II GC
3: PERKIN ELMER 900 GC
4: BECKMAN 6800 THC/CH4
5: CEA FORMALDEHYDE
6: VARIAN GC
7: DNPH ALDEHYDES (QUALITATIVE)

DATA EXCEPTIONS: NONE

CHAMBER CONDITIONS:
1: 24 HOURS OF VENTING
2: DRYING WAS PERFORMED
3: NO CONDENSATION WAS OBSERVED

SPECIAL PROBLEMS OR CONCERNS: NONE

EXPERIMENT STARTS:	0708
INITIAL CONDITIONS ESTABLISHED:	0530
EXPERIMENTS ENDS:	1739

RUN QUALITY INDEX:	9.5/10.0

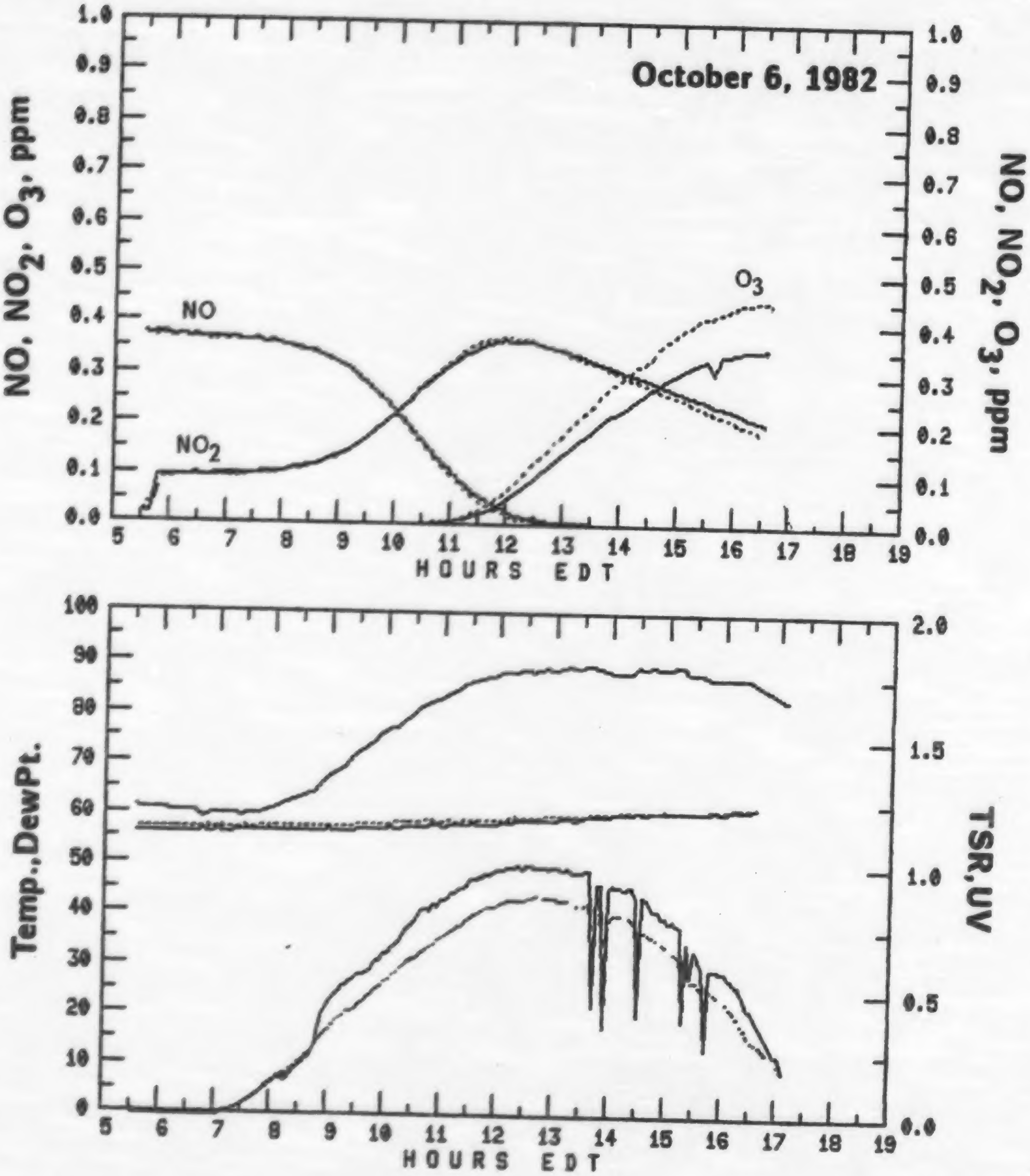


Figure D15. TOP: Dodge Charger, direct injection , NMHC= 1.96 ppmC, (dashed lines); Plymouth Volare, direct injection, NMHC= 1.97 ppmC, (solid lines).
BOTTOM: Chamber air temperature and dew point; ambient total solar and ultraviolet radiation;

Initial Conditions for October 6,1982

			DC/66 BLUE			PV/66 RED		
	Cnum	Split *	PPMC	%C	PPMV	RED	%C	PPMV
PARAFFINS								
ethane	2		0.035	1.79	0.018	0.031	1.57	0.016
propane	3		0.043	2.20	0.014	0.027	1.37	0.009
n-butane	4		0.138	7.06	0.035	0.150	7.61	0.038
i-butane	4		NM	NA	NM	NM	NA	NM
i-pentane	5		0.030	1.53	0.006	0.050	2.54	0.010
n-pentane	5		ND	NA	ND	ND	NA	ND
2-me-pentane	6		0.050	2.56	0.008	0.050	2.54	0.008
trime-pentanes	8		NM	NA	NM	NM	NA	NM
octane	8		NM	NA	NM	NM	NA	NM
C6 unk(C1G)	6		ND	NA	ND	ND	NA	ND
Sub-total			0.296	15.14	0.081	0.308	15.63	0.080
OLEFINS								
ethylene	2		0.275	14.07	0.138	0.250	12.68	0.125
propylene	3		0.134	6.85	0.045	0.114	5.78	0.038
1-butene	4		NM	NA	NM	NM	NA	NM
c-2-butene	4		NM	NA	NM	NM	NA	NM
t-2-butene	4		NM	NA	NM	NM	NA	NM
1,3butadiene	4		NM	NA	NM	NM	NA	NM
2-me-1-butene	5		ND	NA	ND	ND	NA	ND
2-me-2-butene	5		0.030	1.53	0.006	0.030	1.52	0.006
Sub-total			0.439	22.46	0.188	0.394	19.99	0.169

AROMATICS							
benzene	6		0.181	9.26	0.030	0.156	7.91	0.026
toluene	7		0.196	10.03	0.028	0.169	8.57	0.024
mp-xylene	8		0.067	3.43	0.008	0.062	3.15	0.008
et-benzenes	8		0.020	1.02	0.003	0.017	0.86	0.002
pro-benzenes	9		ND	NA	ND	ND	NA	ND
o-xylene	8		0.028	1.43	0.004	0.026	1.32	0.003
135-C3-benzene	9		ND	NA	ND	ND	NA	ND
123-C3-benzene	9		ND	NA	ND	ND	NA	ND
124-C3-benzene	9		0.038	1.94	0.004	0.037	1.88	0.004
dimeet-benzene	10		0.021	1.07	0.002	0.020	1.01	0.002
m-eth-toluene	9		0.034	1.74	0.004	0.033	1.67	0.004
o-eth-toluene	9		ND	NA	ND	ND	NA	ND
styrene	8		ND	NA	ND	ND	NA	ND
napthalene	10		0.031	1.59	0.003	0.035	1.78	0.004
2me-napthalene	11		ND	NA	ND	ND	NA	ND
1me-napthalene	11		ND	NA	ND	ND	NA	ND
others	10	4	0.024	1.23	0.002	0.023	1.17	0.002
Sub-total			0.640	32.74	0.088	0.578	29.33	0.079
ACETYLENE							
acetylene	2		0.359	18.36	0.180	0.287	14.56	0.144
TOTAL MEASURED SPECIES			1.734	88.70	0.536	1.567	79.50	0.472
Unspeciated Carbon			0.221	11.30		0.404	20.50	
FINAL NMHC			1.955			1.971		

```
                                                  |
                                                  |
##################################################|##########################
                                                  |
SUMMARY                                           |
                     PPMC      %C       Car Num   | PPMC      %C       Car Num
                                                  |
     Meas PAR        0.296     15.14      3.67    |  0.308     15.63      3.83
     Est  PAR        0.000      0.00      0.00    |  0.304     15.42      7.90
                 ---------------------------------|---------------------------
     TOT  PAR     5  0.296     15.14      5.15    |  0.612     31.05      5.15
                                                  |
                                                  |
     Meas OLE        0.439     22.46      2.33    |  0.394     19.99      2.33
      Est OLE        0.000      0.00      0.00    |  0.000      0.00      0.00
                 ---------------------------------|---------------------------
      TOT OLE     5  0.439     22.46      2.55    |  0.394     19.99      2.55
                                                  |
                                                  |
     Meas ARO        0.640     32.74      7.26    |  0.578     29.33      7.33
      Est ARO        0.221     11.30     10.26    |  0.100      5.12     13.29
                 ---------------------------------|---------------------------
                  5  0.861     44.04      7.85    |  0.678     34.40      7.85
                                                  |
     Meas ACE        0.359     18.36      2.00    |  0.287     14.56      2.00
                 ---------------------------------|---------------------------
      TOT ACE        0.359     18.36      2.00    |  0.287     14.56      2.00
                                                  |
--------------   ---------------------------------|---------------------------
--------------   ---------------------------------|---------------------------
      Spec HC        1.734     88.70              |  1.567     79.50
    Unspec HC        0.221     11.30              |  0.404     20.50
                 ------------------               |------------------
     TOT NMHC        1.955    100.00              |  1.971    100.00
```

June 17, 1983

Unmatched NMHC/NOx Conditions from Plymouth Volare (BLUE) and Dodge Charger (RED)

INITIAL CONDITIONS:	BLUE	RED
NO	0.523	0.525
NO2	0.159	0.154
PLYMOUTH VOLARE	2.4	0.0
DODGE CHARGER	0.0	1.1
	MORN	AFTERNOON
SUNLIGHT AND WEATHER:	8.0/10	6.5/10
TEMPERATURE F:	67.0	89.0

INSTRUMENTS USED:

1: CARLE I GC

2: CARLE II GC

3: PERKIN ELMER 900 GC

4: BECKMAN 6800 THC/CH4

5: CEA FORMALDEHYDE

6: VARIAN GC

7: DNPH ALDEHYDES (QUALITATIVE)

DATA EXCEPTIONS: ACETALDEHYDE, TSR, UV, TEMP.

SPECIAL PROBLEMS OR CONCERNS:

1: TARGET CONDITIONS WERE FOR MATHCED INITIAL NMHC AND NOX.

2: POOR AFTERNOON SUNLIGHT.

3: LOST COMPUTER FILES OF LIGHT, TEMPERATURE, DEWPOINT, AND NOX AND O3. NOX, O3, AND LIGHT DATA WERE OBTAINED FROM STRIPCHARTS.

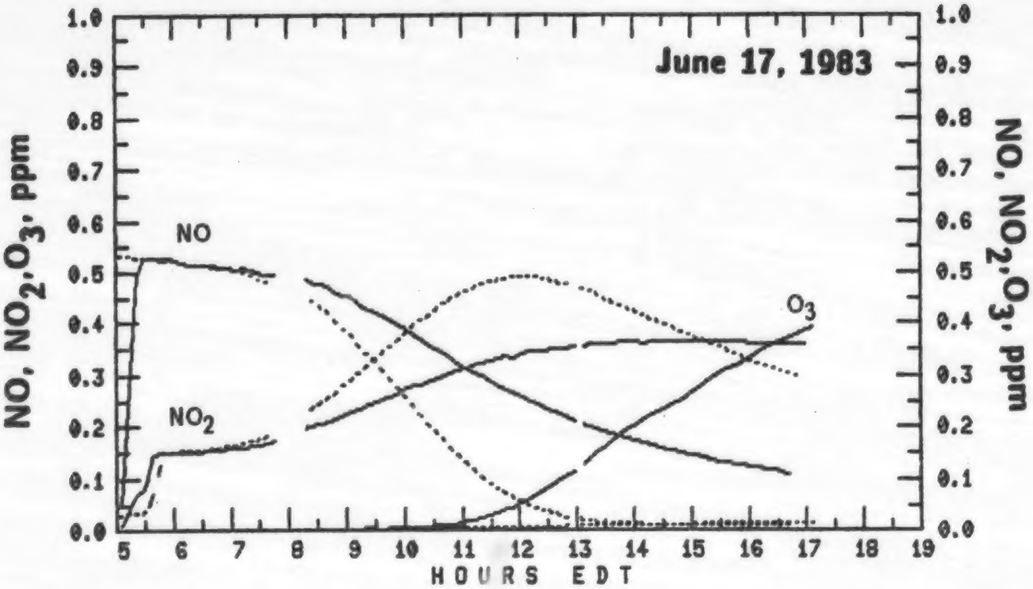
4: EXPERIMENT NOT TO BE PROCESSED.

CHAMBER CONDITIONS:

1: MORE THAN 24 HOURS VENTING.

2: DRYING PERFORMED; NO CHAMBER CONDENSATION OBSERVED.

EXPERIMENT STARTS: SUNRISE -	0550
INITIAL CONDITIONS ESTABLISHED:	0550
EXPERIMENTS ENDS:	1710
RUN QUALITY INDEX:	4.0/10



DATA MISSING

Figure D16. TOP: Plymouth Volare, direct injection , NMHC= 2.4 ppmC, (dashed lines); Dodge Charger, direct injection, NMHC= 1.1 ppmC, (solid lines).

June 29, 1983

EKMA Test : Direct Injections from Dodge Charger to Different Levels of NMHC with Matched NOx.

INITIAL CONDITIONS:	BLUE	RED
NO	0.115	0.105
NO2	0.040	0.035
NMHC	0.8	2.5
CO	4.1	13.8

	MORN	AFTERNOON
SUNLIGHT AND WEATHER:	6.0/10	4.0/10
TEMPERATURE F:	75.0	96.0

INSTRUMENTS USED:

1: CARLE I GC

2: CARLE II GC

3: CARLE III GC

4: PERKIN ELMER 900 GC

5: BECKMAN 6800 THC/CH4

6: CEA FORMALDEHYDE

7: VARIAN GC

DATA EXCEPTIONS:

1: DEWPOINT DATA UNTIL 0915.

2: DNPH ALDEHYDES.

3: ACETALDEHYDE.

SPECIAL PROBLEMS OR CONCERNS:

1: POOR SUNLIGHT.

CHAMBER CONDITIONS:

1: 7 HOURS VENTING.

2: DRYING PERFORMED; NO CHAMBER CONDENSATION OBSERVED.

EXPERIMENT STARTS: SUNRISE -	0553
INITIAL CONDITIONS ESTABLISHED:	0614
EXPERIMENTS ENDS:	1633

RUN QUALITY INDEX:	7.0/10

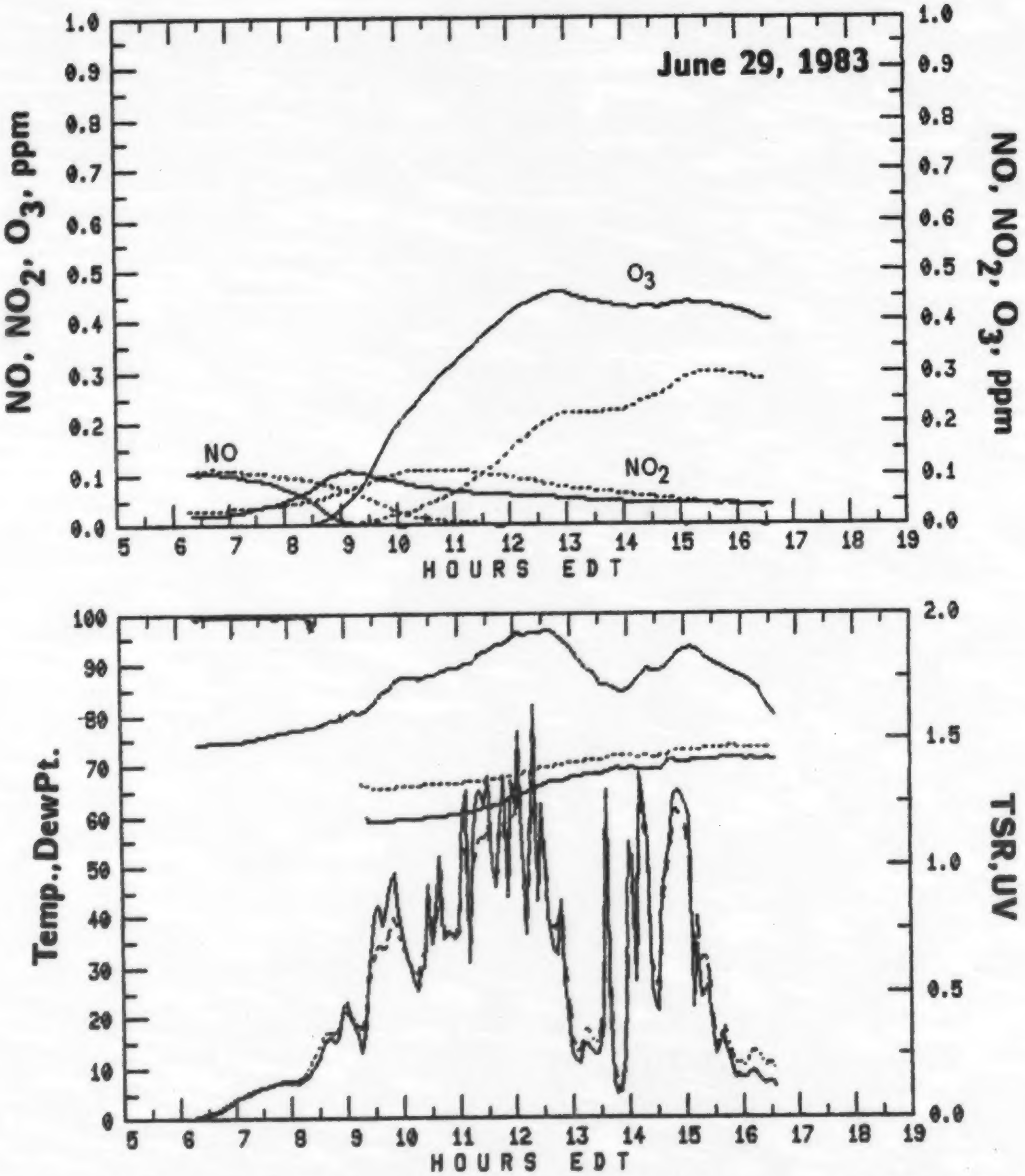


Figure D17. TOP: Dodge Charger, direct injection , NMHC= 0.8 ppmC, (dashed lines); Dodge Charger, direct injection, NMHC= 2.5 ppmC, (solid lines).
BOTTOM: Chamber air temperature and dew point; ambient total solar and ultraviolet radiation;

July 2, 1983

Matched NMHC/NOx Conditions from Plymouth Volare (BLUE) and Dodge Charger (RED)

INITIAL CONDITIONS:	BLUE	RED
NO	0.1623	0.1635
NO2	0.0219	0.014
PLYMOUTH VOLARE, NMHC	1.700	0.0
DODGE CHARGER, NMHC	0.0	1.644
CO	38.6	10.6

	MORN	AFTERNOON
SUNLIGHT AND WEATHER:	8.5/10	7.5/10
TEMPERATURE F:	72.4	99.2

INSTRUMENTS USED:

1: CARLE I GC

2: CARLE II GC

3: PERKIN ELMER 900 GC

4: BECKMAN 6800 THC/CH4

5: CEA FORMALDEHYDE

6: VARIAN GC

DATA EXCEPTIONS:

1: ALKYLNITRATES.

2: DNPH ALDEHYDES.

3: ACETALDEHYDE.

SPECIAL PROBLEMS OR CONCERNS:

1: SOMEWHAT POOR AFTERNOON SUNLIGHT.

CHAMBER CONDITIONS:

1: 76 HOURS VENTING;

2: DRYING PERFORMED BUT SOME CHAMBER CONDENSATION OBSERVED.

EXPERIMENT STARTS: SUNRISE -	0605
INITIAL CONDITIONS ESTABLISHED:	0530
EXPERIMENTS ENDS:	1145 (JULY 3)
RUN QUALITY INDEX:	9.0/10

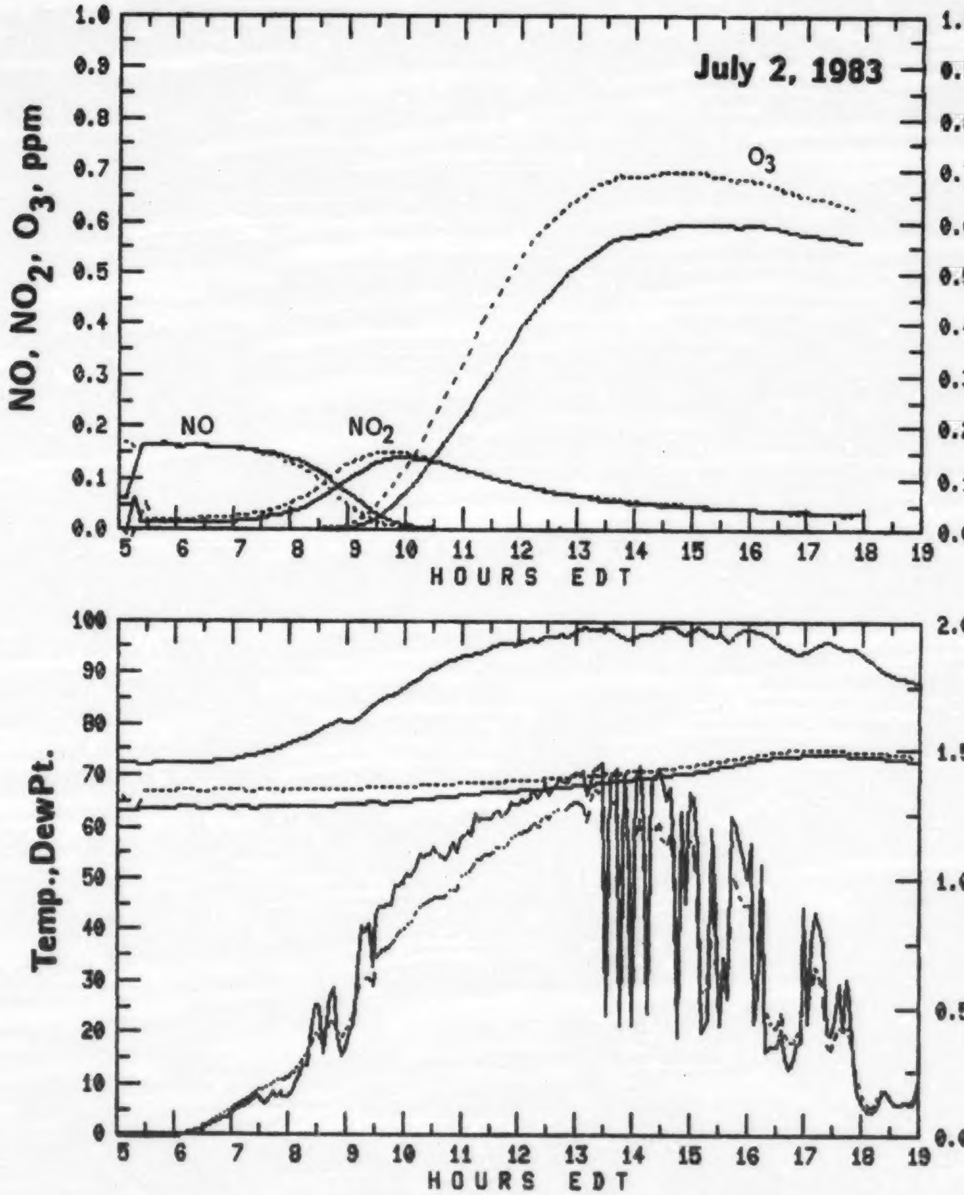


Figure D18. TOP: Plymouth Volare, direct injection , NMHC= 1.70 ppmC, (dashed lines); Dodge Charger, direct injection, NMHC= 1.64 ppmC, (solid lines).
BOTTOM: Chamber air temperature and dew point; ambient total solar and ultraviolet radiation;

Initial Conditions for July 2, 1983

				PV/66			DC/66		
				BLUE			RED		
	Cnum	Split	*	PPMC	%C	PPMV	RED	%C	PPMV
PARAFFINS									
ethane	2			0.023	1.35	0.012	0.024	1.46	0.012
propane	3			0.023	1.35	0.008	0.016	0.97	0.005
n-butane	4	0.66	1	0.027	1.56	0.007	0.031	1.86	0.008
i-butane	4	0.18	1	0.007	0.42	0.002	0.008	0.50	0.002
i-pentane	5			0.031	1.82	0.006	0.066	4.01	0.013
n-pentane	5			0.024	1.41	0.005	0.036	2.19	0.007
2-me-pentane	6			0.015	0.88	0.003	0.015	0.91	0.003
trime-pentanes	8			NM	NA	NM	NM	NA	NM
octane	8			NM	NA	NM	NM	NA	NM
C6 unk(C1G)	6			0.031	1.82	0.005	0.029	1.76	0.005
Sub-total				0.181	10.63	0.046	0.225	13.67	0.055
OLEFINS									
ethylene	2			0.170	10.00	0.085	0.092	5.59	0.046
propylene	3			0.072	4.24	0.024	0.039	2.37	0.013
1-butene	4	0.16	1	0.006	0.37	0.002	0.007	0.44	0.002
c-2-butene	4	0.19	2	0.008	0.48	0.002	0.005	0.31	0.001
t-2-butene	4	0.06	2	0.003	0.16	0.001	0.002	0.10	.000
1,3butadiene	4	0.74	2	0.032	1.88	0.008	0.020	1.22	0.005
2-me-1-butene	5			ND	NA	ND	ND	NA	ND
2-me-2-butene	5			ND	NA	ND	ND	NA	ND
Sub-total				0.291	17.14	0.121	0.165	10.05	0.068

AROMATICS								
benzene	6		0.102	6.00	0.017	0.075	4.56	0.013
toluene	7		0.202	11.88	0.029	0.217	13.20	0.031
mp-xylene	8		0.069	4.06	0.009	0.060	3.65	0.008
et-benzenes	8		0.018	1.06	0.002	0.020	1.22	0.003
pro-benzenes	9		0.011	0.65	0.001	0.014	0.85	0.002
o-xylene	8		0.030	1.76	0.004	0.029	1.76	0.004
135-C3-benzene	9		0.011	0.65	0.001	0.011	0.67	0.001
123-C3-benzene	9		ND	NA	ND	ND	NA	ND
124-C3-benzene	9		0.039	2.29	0.004	0.040	2.43	0.004
dimeet-benzene	10		0.012	0.71	0.001	0.015	0.91	0.002
m-eth-toluene	9		0.018	1.06	0.002	0.022	1.34	0.002
o-eth-toluene	9		0.007	0.41	0.001	0.008	0.49	0.001
styrene	8		0.011	0.65	0.001	0.008	0.49	0.001
napthalene	10		0.021	1.24	0.002	0.014	0.85	0.001
2me-napthalene	11		0.006	0.35	0.001	0.004	0.24	ND
1me-napthalene	11		0.003	0.18	ND	0.003	0.18	ND
others	10	4	0.072	4.24	0.007	0.066	4.01	0.007
Sub-total			0.632	37.18	0.083	0.606	36.85	0.079
ACETYLENE								
acetylene	2		0.145	8.53	0.073	0.128	7.78	0.064
TOTAL MEASURED SPECIES			1.249	73.47	0.323	1.124	68.35	0.265
Unspeciated Carbon			0.451	26.53		0.520	31.65	
FINAL NMHC			1.700			1.644		

```
                                                         |
                                                         |

#########################################################|#############################
                                                         |
SUMMARY                                                  |
                              PPMC      %C      Car Num  |  PPMC       %C      Car Num
                                                         |
     Meas PAR                  0.181     10.63      3.91 |   0.225     13.67      4.10
     Est  PAR                  0.251     14.77      6.68 |   0.220     12.94      6.96
                            -----------------------------|-----------------------------
     TOT  PAR              5   0.432     25.39      5.15 |   0.445     26.16      5.15
                                                         |
                                                         |
     Meas OLE                  0.291     17.14      2.40 |   0.165     10.05      2.45
      Est OLE                  0.100      5.88      3.11 |   0.200     11.77      2.64
                            -----------------------------|-----------------------------
      TOT OLE              5   0.391     23.02      2.55 |   0.365     21.49      2.55
                                                         |
                                                         |
     Meas ARO                  0.632     37.18      7.64 |   0.606     35.85      7.69
      Est ARO                  0.100      5.88      9.51 |   0.100      5.88      8.99
                            -----------------------------|-----------------------------
                           5   0.732     43.06      7.85 |   0.706     41.53      7.85
                                                         |
     Meas ACE                  0.145      8.53      2.00 |   0.128      7.78      2.00
                            -----------------------------|-----------------------------
      TOT ACE                  0.145      8.53      2.00 |   0.128      7.78      2.00
                                                         |
---------------             -----------------------------|-----------------------------
---------------             -----------------------------|-----------------------------
      Spec HC                  1.249     73.47           |   1.124     68.35
    Unspec HC                  0.451     26.53           |   0.520     31.62
                            --------------------         |--------------------
     TOT NMHC                  1.700    100.01           |   1.644     99.98
```

July 8, 1983

Matched Direct Injections from Plymouth Volare (BLUE) and Dodge Charger (RED)

INITIAL CONDITIONS:	BLUE	RED
NO	0.306	0.308
NO2	0.062	0.064
PLYMOUTH VOLARE NMHC	1.687	0.0
DODGE CHARGER NMHC	0.0	1.726
CO	28.4	13.4

	MORN	AFTERNOON
SUNLIGHT AND WEATHER:	10/10	10/10
TEMPERATURE F:	55	91

INSTRUMENTS USED:

1: CARLE I GC
2: CARLE II GC
3: PERKIN ELMER 900 GC
4: BECKMAN 6800 THC/CH4
5: CEA FORMALDEHYDE
6: VARIAN GC

DATA EXCEPTIONS:

1: DNPH ALDEHYDES
2: GC-FID ACETALDEHYDE.

SPECIAL PROBLEMS OR CONCERNS:

1: VERY COOL MORNING; NO CONDENSATION OBSERVED.
2: FINAL NOX INJECTIONS COMPLETED JUST AFTER SUNRISE (ABOUT 10 MIN).

CHAMBER CONDITIONS:

1: CHAMBER DID NOT PROPERLY VENT DURING NIGHT. VENTED MANUALLY. HOURS OF VENTING BEFORE RUN 2 HRS.
2: DRYING PERFORMED; NO CONDENSATION OBSERVED.

EXPERIMENT STARTS:	0618
INITIAL CONDITIONS ESTABLISHED:	0555
EXPERIMENTS ENDS:	1710

RUN QUALITY INDEX:	9/10

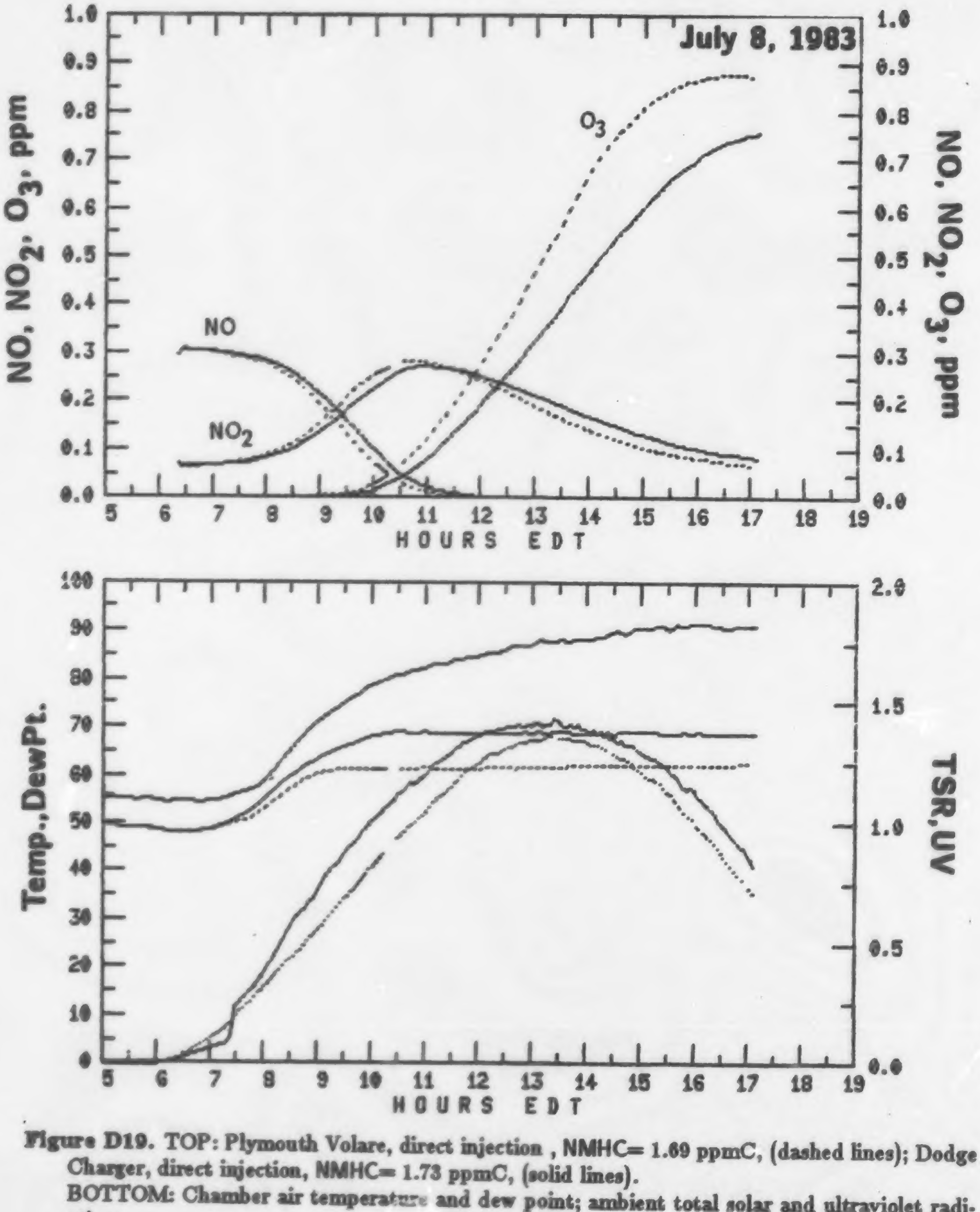


Figure D19. TOP: Plymouth Volare, direct injection , NMHC= 1.69 ppmC, (dashed lines); Dodge Charger, direct injection, NMHC= 1.73 ppmC, (solid lines).
BOTTOM: Chamber air temperature and dew point; ambient total solar and ultraviolet radiation;

July 15, 1983

Direct Injections from Dodge Charger Fueled with Phillips 66 Unleaded Regular (BLUE) and Amoco Premium (RED)

INITIAL CONDITIONS:	BLUE	RED
NO	0.307	0.314
NO2	0.045	0.045
REGULAR, NMHC	2.25	0.0
PREMIUM, NMHC	0.0	2.19
CO	12.37	2.91

	MORN	AFTERNOON
SUNLIGHT AND WEATHER:	9/10	9.6/10
TEMPERATURE F:	74.1	101.6

INSTRUMENTS USED:

1: CARLE I GC
2: CARLE II GC
3: PERKIN ELMER 900 GC
4: BECKMAN 6800 THC/CH4
5: CEA FORMALDEHYDE
6: VARIAN GC

DATA EXCEPTIONS:

1: ACETALDEHYDE.
2: DNPH ALDEHYDES.

SPECIAL PROBLEMS OR CONCERNS: NONE

CHAMBER CONDITIONS:

1: NORMAL VENTING.
2: DRYING PERFORMED; NO CHAMBER CONDENSATION OBSERVED.

EXPERIMENT STARTS: SUNRISE -	0608
INITIAL CONDITIONS ESTABLISHED:	0545
EXPERIMENTS ENDS:	1628

RUN QUALITY INDEX: 9.8/10

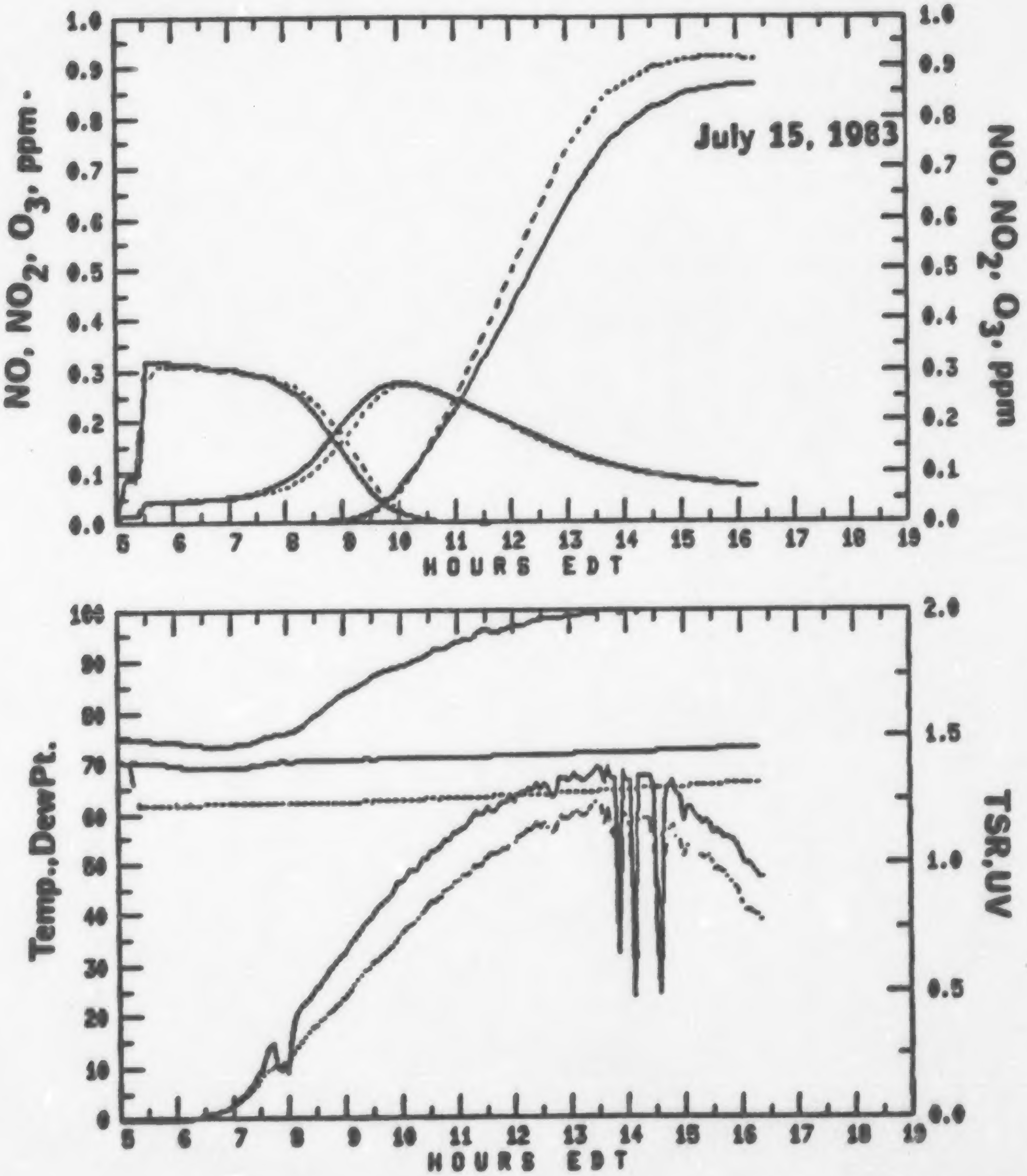


Figure D20. TOP: Dodge Charger, regular gas, direct injection , NMHC= 2.25 ppmC, (dashed lines); Dodge Charger, premium gas, direct injection, NMHC= 2.19 ppmC, (solid lines). BOTTOM: Chamber air temperature and dew point; ambient total solar and ultraviolet radiation;

Initial Conditions for July 15, 1983

	Cnum	Split	*	DC/66 BLUE PPMC	%C	PPMV	DC/AMO RED RED	%C	PPMV
PARAFFINS									
ethane	2			0.010	0.44	0.005	0.010	0.51	0.005
propane	3			0.015	0.67	0.005	ND	NA	ND
n-butane	4	0.66	1	0.044	1.97	0.011	0.056	2.83	0.014
i-butane	4	0.18	1	0.012	0.53	0.003	0.015	0.76	0.004
i-pentane	5			0.098	4.36	0.020	0.143	7.27	0.029
n-pentane	5		6	ND	NA	ND	ND	NA	ND
2-me-pentane	6		6	ND	NA	ND	ND	NA	ND
trime-pentanes	8			NM	NA	NM	NM	NA	NM
octane	8			NM	NA	NM	NM	NA	NM
C6 unk(C1G)	6		6	ND	NA	ND	ND	NA	ND
Sub-total				0.179	7.97	0.044	0.224	11.37	0.051
OLEFINS									
ethylene	2			0.199	8.84	0.100	0.114	5.79	0.057
propylene	3			0.104	4.62	0.035	0.081	4.12	0.027
1-butene	4	0.16	1	0.011	0.47	0.003	0.013	0.67	0.003
c-2-butene	4	0.19	2	0.008	0.36	0.002	0.008	0.42	0.002
t-2-butene	4	0.06	2	0.003	0.12	0.001	0.003	0.14	0.001
1,3butadiene	4	0.74	2	0.031	1.39	0.008	0.032	1.63	0.008
2-me-1-butene	5		6	ND	NA	ND	ND	NA	ND
2-me-2-butene	5		6	ND	NA	ND	ND	NA	ND
Sub-total				0.356	15.80	0.147	0.251	12.77	0.098

```
                                                     |
AROMATICS                                            |
                                                     |
     benzene   6           0.141    6.25    0.023 |  0.100    5.08    0.017
     toluene   7           0.292   12.98    0.042 |  0.327   16.62    0.047
   mp-xylene   8           0.092    4.09    0.012 |  0.098    4.98    0.012
  et-benzenes  8           0.035    1.56    0.004 |  0.045    2.29    0.006
 pro-benzenes  9           0.010    0.44    0.001 |  0.012    0.61    0.001
    o-xylene   8           0.047    2.09    0.006 |  0.052    2.64    0.007
135-C3-benzene 9           0.021    0.93    0.002 |  0.015    0.76    0.002
123-C3-benzene 9           0.040    1.78    0.004 |  0.052    2.64    0.006
124-C3-benzene 9           0.075    3.33    0.008 |  0.067    3.40    0.007
dimeet-benzene 10          0.014    0.62    0.001 |  0.003    0.15     .000
m-eth-toluene  9           0.029    1.29    0.003 |  0.026    1.32    0.003
o-eth-toluene  9           0.014    0.62    0.002 |  0.013    0.66    0.001
     styrene   8           0.011    0.49    0.001 |  0.006    0.30    0.001
   napthalene  10          0.026    1.16    0.003 |  0.019    0.97    0.002
2me-napthalene 11          0.007    0.31    0.001 |  0.004    0.20     .000
1me-napthalene 11          0.005    0.22     .000 |  0.006    0.30    0.001
      others   10       4  0.110    4.89    0.011 |  0.093    4.73    0.009
--------------------------------------------------|--------------------------
Sub-total                  0.969   43.05    0.125 |  0.938   47.66    0.121


                                                  |
ACETYLENE                                         |
                                                  |
   acetylene   2           0.137    6.09    0.069 |  0.039    1.98    0.020
==================================================|==========================
                                                  |
TOTAL MEASURED SPECIES     1.641   72.92    0.385 |  1.452   73.78    0.290
                                                  |
Unspeciated Carbon         0.609   27.08          |  0.516   26.22
                                                  |
FINAL NMHC                 2.250                  |  1.968
```

```
                                                      |
                                                      |
#####################################################|##########################
                                                      |
SUMMARY                                               |
                           PPMC      %C     Car Num  |  PPMC       %C     Car Num
                                                      |
      Meas PAR             0.179     7.97      4.11  |  0.224     11.37      4.36
      Est  PAR             0.350    15.56      5.92  |  0.300     13.33      5.95
                         ----------------------------|---------------------------
      TOT  PAR        5    0.529    23.53      5.15  |  0.524     23.28      5.15
                                                      |
                                                      |
      Meas OLE             0.356    15.80      2.41  |  0.251     12.77      2.56
       Est OLE             0.159     7.07      2.92  |  0.108      4.80      2.52
                         ----------------------------|---------------------------
       TOT OLE        5    0.515    22.87      2.55  |  0.359     15.97      2.55
                                                      |
                                                      |
      Meas ARO             0.969    43.05      7.73  |  0.938     47.66      7.72
       Est ARO             0.100     4.44      9.29  |  0.108      4.80      9.17
                         ----------------------------|---------------------------
                      5    1.069    47.49      7.85  |  1.046     46.49      7.85
                                                      |
      Meas ACE             0.137     6.09      2.00  |  0.039      1.98      2.00
                         ----------------------------|---------------------------
       TOT ACE             0.137     6.09      2.00  |  0.039      1.98      2.00
                                                      |
--------------           ----------------------------|---------------------------
--------------           ----------------------------|---------------------------
       Spec HC             1.641    72.92            |  1.452     73.78
     Unspec HC             0.609    27.07            |  0.516     26.22
                         ------------------          |------------------
      TOT NMHC             2.250    99.98            |  1.968    100.00
```

July 22, 1983

Matched Direct Injections from Dodge Charger Fueled with Phillips 66 Unleaded Regular (BLUE) and Amoco Premium (RED)

INITIAL CONDITIONS:	BLUE	RED
NO	0.207	0.208
NO2	0.067	0.059
REGULAR NMHC	1.86	0.0
PREMIUM NMHC	0.0	1.81
CO	8.45	1.63

	MORN	AFTERNOON
SUNLIGHT AND WEATHER:	7.5/10	3.0/10
TEMPERATURE F:	75.0	93.0

INSTRUMENTS USED:

1: CARLE I GC
2: CARLE II GC
3: CARLE III GC
4: PERKIN ELMER 900 GC
5: BECKMAN 6800 THC/CH4
6: CEA FORMALDEHYDE
7: VARIAN GC
8: DNPH ALDEHYDES (QUALITATIVE)

DATA EXCEPTIONS:

1: ACETALDEHYDE
2: DNPH ALDEHYDES

SPECIAL PROBLEMS OR CONCERNS:

1: BAD SUN JUST BEFORE NOON AND VERY POOR AFTERNOON SUN.
2: PROBLEMS WITH DVM DATA.
3: EXPERIMENT NOT TO BE PROCESSED.
4: CRYO SAMPLES TAKEN FOR GC/MS ANALYSIS.

CHAMBER CONDITIONS:

1: HOURS OF VENTING BEFORE RUN MORE THAN 6 HRS.
2: DRYING PERFORMED; NO CONDENSATION OBSERVED.

EXPERIMENT STARTS: 0610
INITIAL CONDITIONS ESTABLISHED: 0545
EXPERIMENTS ENDS: 1640

RUN QUALITY INDEX: 4.0/10

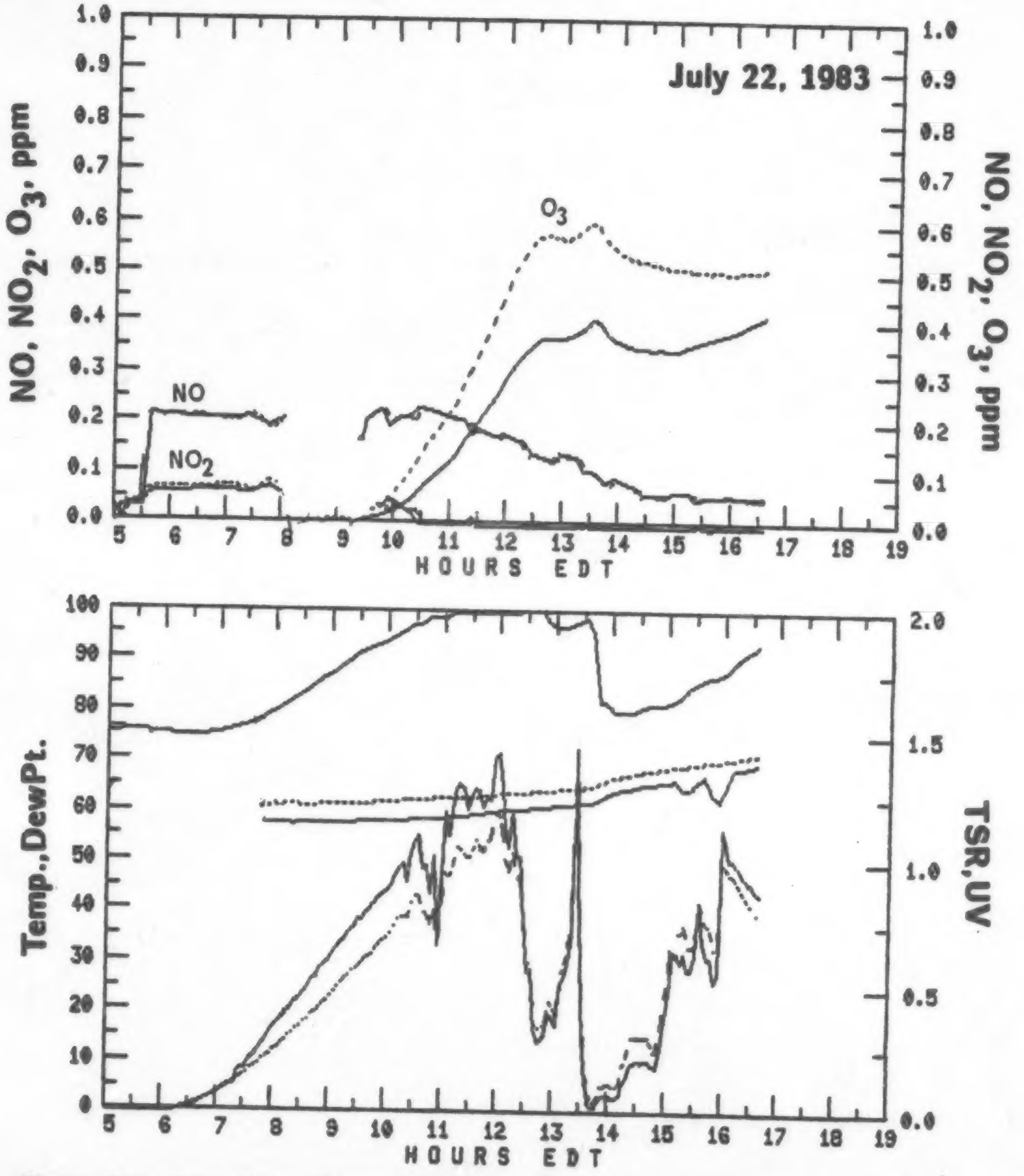


Figure D21. TOP: Dodge Charger, regular gas, direct injection , NMHC= 1.86 ppmC, (dashed lines); Dodge Charger, premium gas, direct injection, NMHC= 1.81 ppmC, (solid lines). BOTTOM: Chamber air temperature and dew point; ambient total solar and ultraviolet radiation;

July 25, 1983

Matched Simple Synthetic Automobile Exhaust

INITIAL CONDITIONS:	BLUE	RED
NO	0.210	0.222
NO2	0.035	0.038
ETHYLENE	1.124	1.183
PROPYLENE	0.600	0.656
ISOPENTANE	0.164	0.164
TOLUENE	0.593	0.593
1,2,4-TRIMETHYLBENZENE	0.364	0.364
SYNTHETIC EXHAUST NMHC	2.845	2.960

	MORN	AFTERNOON
SUNLIGHT AND WEATHER:	7.5/10	1.0/10
TEMPERATURE F:	72.0	95.5

INSTRUMENTS USED:
1: CARLE I GC
2: CARLE II GC
3: PERKIN ELMER 900 GC
4: BECKMAN 6800 THC/CH4
5: CEA FORMALDEHYDE
6: VARIAN GC

DATA EXCEPTIONS: NONE.

SPECIAL PROBLEMS OR CONCERNS:
1: POOR AFTERNOON SUN; FAIR MORNING SUN.

CHAMBER CONDITIONS:
1: 9 HOURS VENTING.
2: DRYING PERFORMED; NO CHAMBER CONDENSATION OBSERVED.

EXPERIMENT STARTS: SUNRISE -	0610
INITIAL CONDITIONS ESTABLISHED: BEFORE SR	0500
EXPERIMENTS ENDS:	1800

RUN QUALITY INDEX: 7.5/10

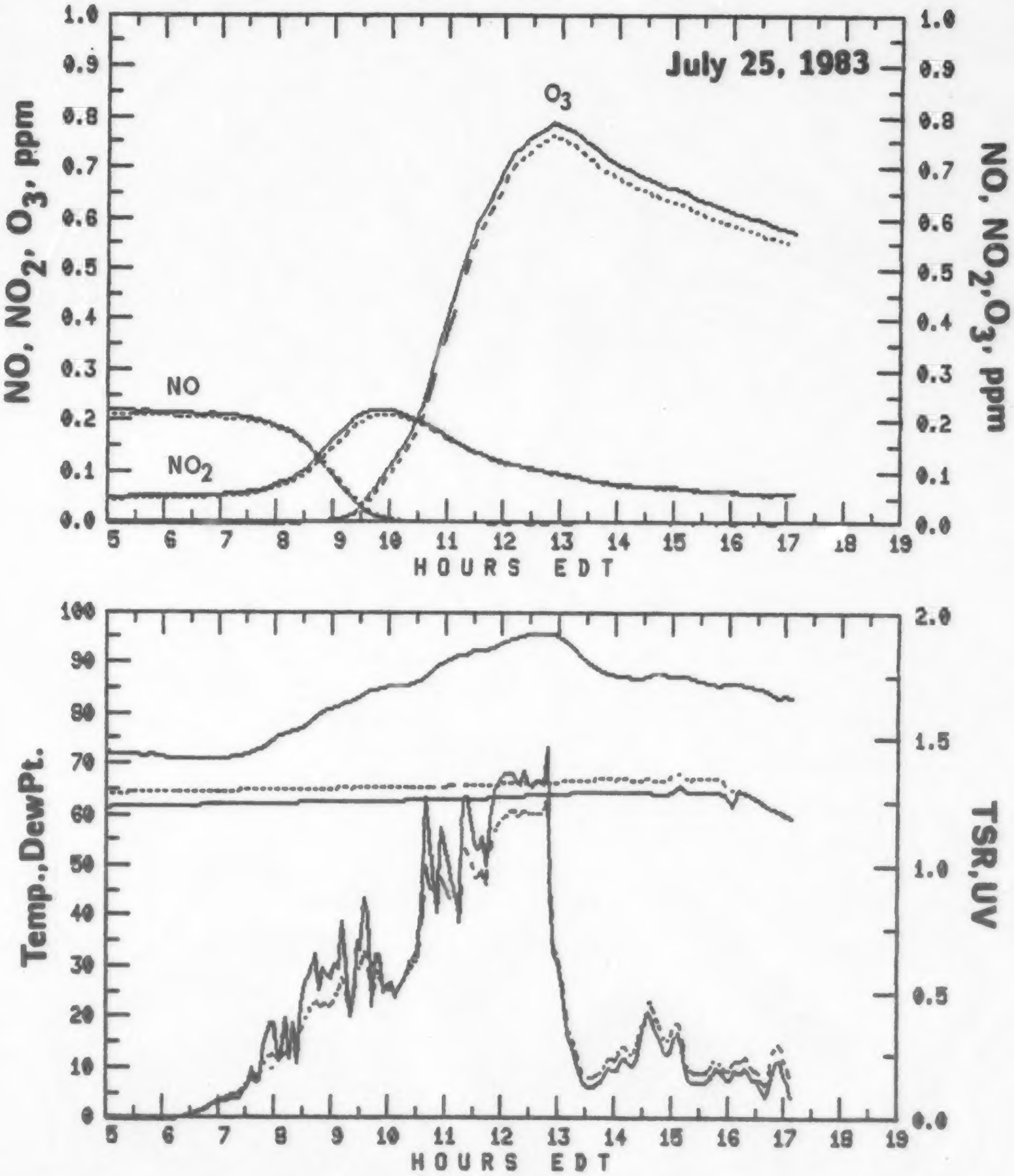


Figure D22. TOP: Matched Simple Synthetic Auto Exhaust, NMHC= 2.85 ppmC, (dashed lines); NMHC= 2.96 ppmC, (solid lines).
BOTTOM: Chamber air temperature and dew point; ambient total solar and ultraviolet radiation;

July 28, 1983

Matched Direct Injections from Dodge Charger Fueled with Phillips 66 Unleaded Regular (BLUE) and Amoco Premium (RED)

INITIAL CONDITIONS:	BLUE	RED
NO	0.288	0.289
NO2	0.036	0.038
REGULAR NMHC	2.52	0.0
PREMIUM NMHC	0.0	2.50
CO	1.44	10.8

	MORN	AFTERNOON
SUNLIGHT AND WEATHER:	9.0/10	9.0/10
TEMPERATURE F:	62.0	94.0

INSTRUMENTS USED:

1: CARLE I GC
2: CARLE II GC
3: CARLE III GC
4: PERKIN ELMER 900 GC
5: BECKMAN 6800 THC/CH4
6: CEA FORMALDEHYDE
7: VARIAN GC
8: DNPH ALDEHYDES (QUALITATIVE)

DATA EXCEPTIONS: DNPH ALDEHYDES.

SPECIAL PROBLEMS OR CONCERNS:

1: CRYO SAMPLES TAKEN FOR GC/MS ANALYSIS.
2: DEWPOINT METER NOT READING CORRECTLY AT START

CHAMBER CONDITIONS:

1: 7.5 HOURS OF VENTING BEFORE RUN.
2: DRYING PERFORMED; NO CONDENSATION OBSERVED.

EXPERIMENT STARTS:	0616
INITIAL CONDITIONS ESTABLISHED:	0501
EXPERIMENTS ENDS:	1710
RUN QUALITY INDEX:	9.7/10

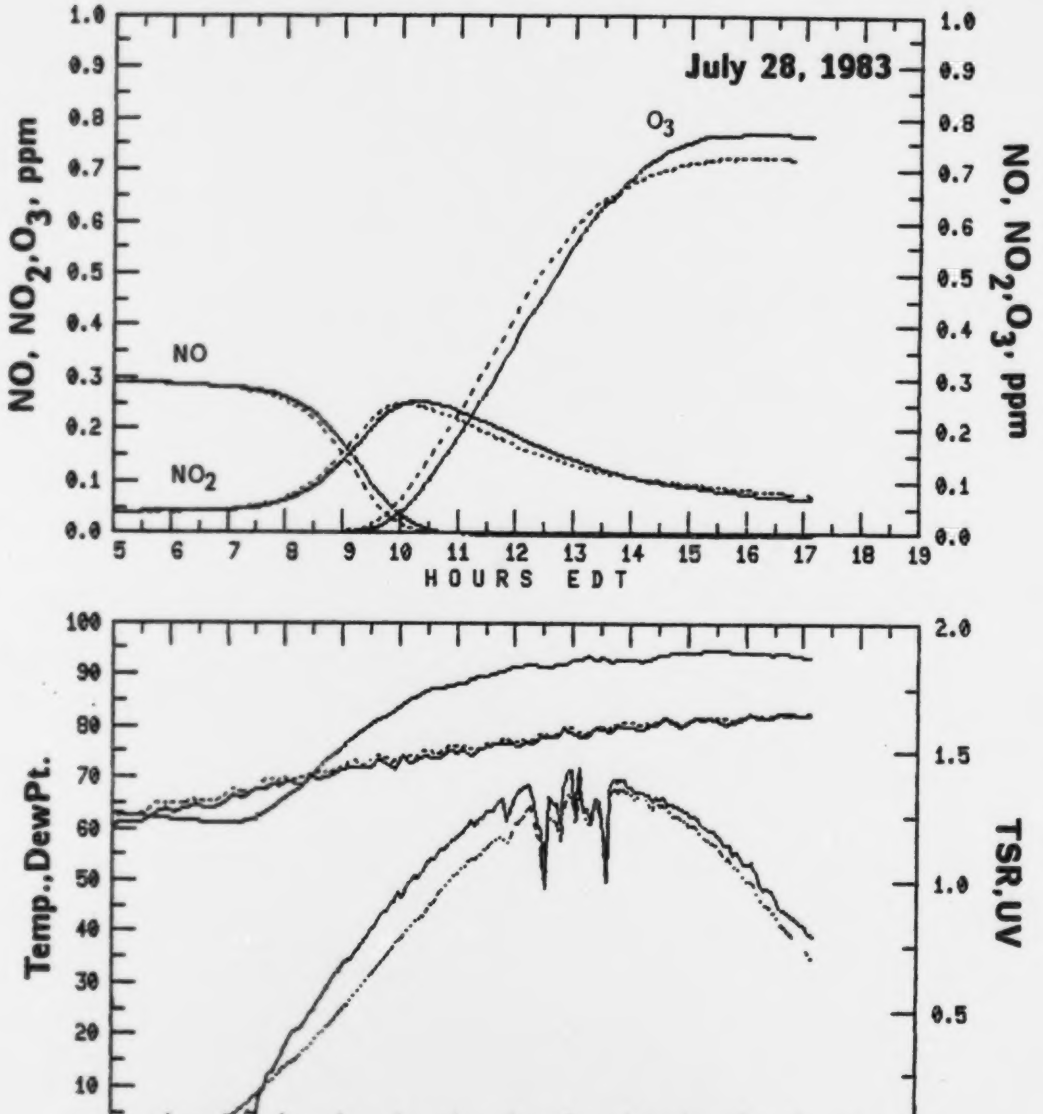


Figure D23. TOP: Dodge Charger, regular gas, direct injection , NMHC= 2.5 ppmC, (dashed lines); Dodge Charger, premium gas, direct injection, NMHC= 2.5 ppmC, (solid lines). BOTTOM: Chamber air temperature and dew point; ambient total solar and ultraviolet radiation;

August 11, 1983

EKMA Test : Direct Injections from Plymouth Volare to Different Levels of NMHC with Matched NOx

INITIAL CONDITIONS:	BLUE	RED
NO	0.183	0.181
NO2	0.043	0.038
NMHC	0.678	2.151
CO	17.1	57.3

	MORN	AFTERNOON
SUNLIGHT AND WEATHER:	9.0/10	8.0/10
TEMPERATURE F:	74.5	102.2

INSTRUMENTS USED:

1: CARLE I GC
2: CARLE II GC
3: CARLE III GC
4: PERKIN ELMER 900 GC
5: BECKMAN 6800 THC/CH4
6: CEA FORMALDEHYDE
7: VARIAN GC

DATA EXCEPTIONS:

1: ALKYLNITRATES
2: ACETALDEHYDE
3: DNPH ALDEHYDES

SPECIAL PROBLEMS OR CONCERNS: NONE

CHAMBER CONDITIONS:

1: MORE THAN 24 HOURS OF VENTING BEFORE RUN.
2: DRYING PERFORMED; NO CONDENSATION OBSERVED.

EXPERIMENT STARTS:	0630
INITIAL CONDITIONS ESTABLISHED:	0520
EXPERIMENTS ENDS:	1800

RUN QUALITY INDEX:	9.0/10.0

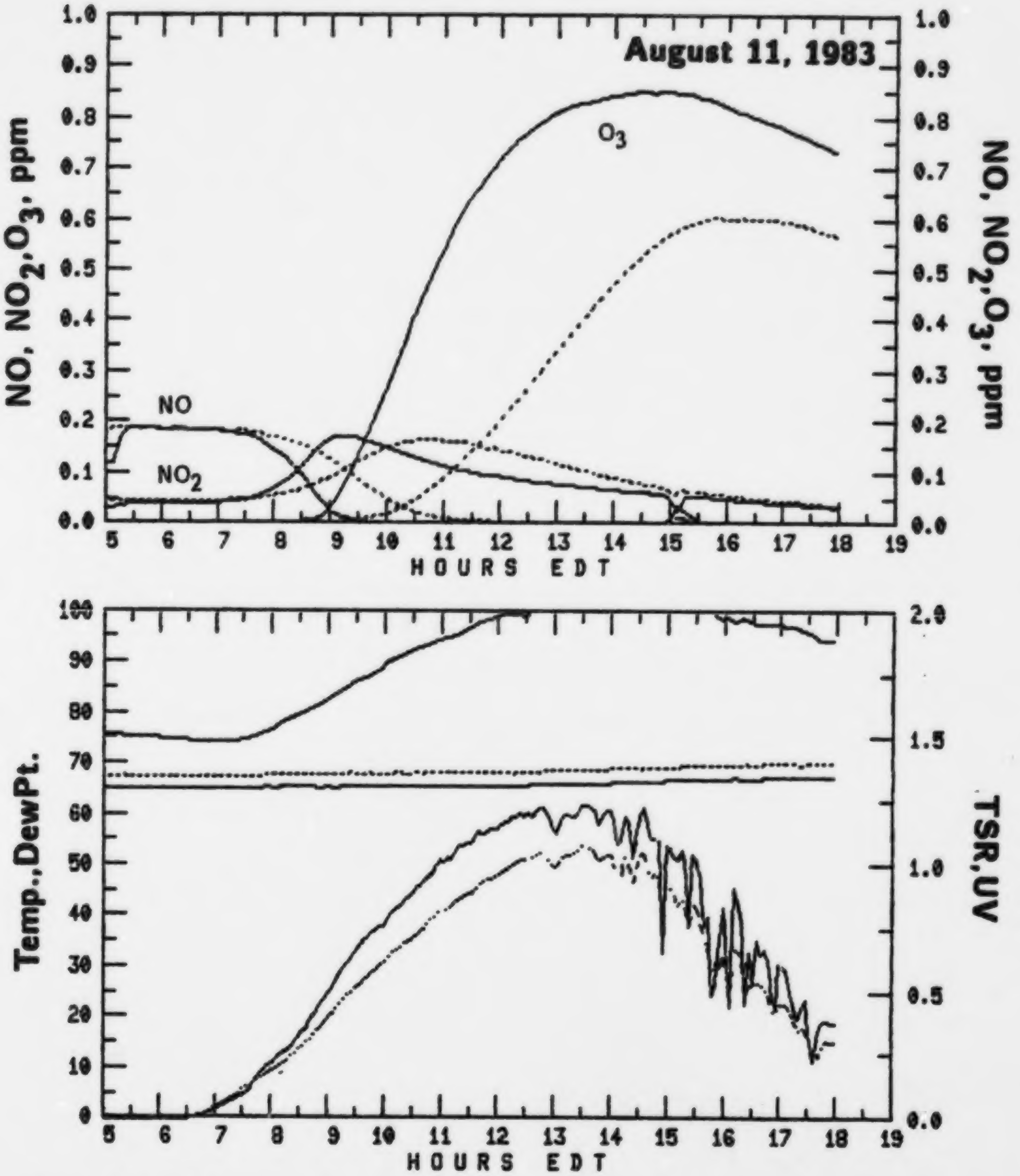


Figure D24. TOP: Plymouth Volare, direct injection , NMHC= 0.68 ppmC, (dashed lines); Plymouth Volare, direct injection, NMHC= 2.15 ppmC, (solid lines).
BOTTOM: Chamber air temperature and dew point; ambient total solar and ultraviolet radiation;

Initial Conditions for August 11, 1983

			PV/66			PV/66		
			BLUE			RED		
	Cnum	Split *	PPMC	%C	PPMV	RED	%C	PPMV
PARAFFINS								
ethane	2		0.012	1.77	0.006	0.034	1.58	0.017
propane	3		ND	NA	ND	ND	NA	ND
n-butane	4		T	NA	T	T	NA	T
i-butane	4		NM	NA	NM	NM	NA	NM
i-pentane	5		ND	NA	ND	0.041	1.91	0.008
n-pentane	5		ND	NA	ND	0.001	0.05	.000
2-me-pentane	6		ND	NA	ND	ND	NA	ND
trime-pentanes	8		ND	NA	ND	0.001	0.05	.000
octane	8		0.001	0.15	.000	0.005	0.23	0.001
C6 unk(C1G)	6		ND	NA	ND	0.030	1.39	0.005
Sub-total			0.013	1.92	0.006	0.112	5.21	0.031
OLEFINS								
ethylene	2		0.119	17.55	0.060	0.375	17.43	0.188
propylene	3		0.050	7.37	0.017	0.143	6.65	0.048
1-butene	4		T	NA	T	0.015	0.70	0.004
c-2-butene	4		T	NA	T	0.009	0.42	0.002
t-2-butene	4		T	NA	T	0.003	0.14	0.001
1,3butadiene	4		T	NA	T	0.035	1.63	0.009
2-me-1-butene	5		ND	NA	ND	0.008	0.37	0.002
2-me-2-butene	5		ND	NA	ND	ND	NA	ND
Sub-total			0.169	24.93	0.076	0.588	27.34	0.252

AROMATICS								
benzene	6		0.061	9.00	0.010	0.179	8.32	0.030
toluene	7		0.141	20.80	0.020	0.315	14.64	0.045
mp-xylene	8		0.044	6.49	0.006	0.139	6.46	0.017
et-benzenes	8		0.012	1.77	0.002	0.040	1.86	0.005
pro-benzenes	9		0.003	0.44	.000	0.007	0.33	0.001
o-xylene	8		0.018	2.65	0.002	0.057	2.65	0.007
135-C3-benzene	9		0.008	1.18	0.001	0.023	1.07	0.003
123-C3-benzene	9		0.010	1.47	0.001	0.011	0.51	0.001
124-C3-benzene	9		0.020	2.95	0.002	0.066	3.07	0.007
dimeet-benzene	10		0.008	1.18	0.001	0.024	1.12	0.002
m-eth-toluene	9		0.010	1.47	0.001	0.030	1.39	0.003
o-eth-toluene	9		0.005	0.74	0.001	0.013	0.60	0.001
styrene	8		0.008	1.18	0.001	0.027	1.26	0.003
napthalene	10		0.012	1.77	0.001	0.030	1.39	0.003
2me-napthalene	11		0.004	0.59	.000	0.010	0.46	0.001
1me-mapthalene	11		0.002	0.29	.000	0.005	0.23	.000
others	10	4	ND	NA	ND	0.052	2.42	0.005
Sub-total			0.366	53.98	0.049	1.028	47.79	0.136
ACETYLENE								
acetylene	2		0.075	11.06	0.038	0.217	10.09	0.109
TOTAL MEASURED SPECIES			0.623	91.89	0.169	1.945	90.42	0.528
Unspeciated Carbon			0.055	8.11		0.206	9.58	
FINAL NMHC			0.678			2.151		

```
                                                 |
                                                 |

#################################################|#########################
                                                 |
SUMMARY                                          |
                          PPMC      %C    Car Num | PPMC     %C     Car Num
                                                 |
    Meas PAR              0.013     1.92    2.12 | 0.112    5.21     3.60
    Est  PAR              0.055     8.11    7.77 | 0.206    9.58     6.73
                        -------------------------|-------------------------
    TOT  PAR           5  0.068    10.03    5.15 | 0.318   14.78     5.15
                                                 |
                                                 |
    Meas OLE              0.169    24.93    2.22 | 0.588   27.34     2.33
     Est OLE              0.000     0.00    0.00 | 0.000    0.00     0.00
                        -------------------------|-------------------------
     TOT OLE           5  0.169    24.93    2.55 | 0.588   27.34     2.55
                                                 |
                                                 |
    Meas ARO              0.366    53.98    7.42 | 1.028   47.79     7.54
     Est ARO              0.000     0.00    0.00 | 0.000    0.00     0.00
                        -------------------------|-------------------------
                       5  0.366    53.98    7.85 | 1.028   47.79     7.85
                                                 |
    Meas ACE              0.075    11.06    2.00 | 0.217   10.09     2.00
                        -------------------------|-------------------------
     TOT ACE              0.075    11.06    2.00 | 0.217   10.09     2.00
                                                 |
-------------           -------------------------|-------------------------
-------------           -------------------------|-------------------------
     Spec HC              0.623    91.89         | 1.945   90.42
   Unspec HC              0.055     8.11         | 0.206    9.58
                        -----------------        |-----------------
    TOT NMHC              0.678   100.00         | 2.151   100.00
```

September 2, 1983

Synthetic Automobile Exhaust (BLUE) vs Direct Injection from Dodge Charger

INITIAL CONDITIONS:	BLUE	RED
NO	0.234	0.235
NO2	0.044	0.041
DODGE CHARGER	0.0	3.0
SYNTHETIC EXHAUST NMHC	2.4	0.0

	MORN	AFTERNOON
SUNLIGHT AND WEATHER:	2.0/10	3.0/10
TEMPERATURE F:	74.0	79.0

INSTRUMENTS USED:

1: CARLE I GC

2: CARLE II GC

3: CARLE III GC

4: PERKIN ELMER 900 GC

5: BECKMAN 6800 THC/CH4

6: CEA FORMALDEHYDE

7: VARIAN GC

8: DNPH ALDEHYDES (QUALITATIVE)

SPECIAL PROBLEMS OR CONCERNS:

1: VERY POOR SUN.

2: CONDENSATION NOT OBSERVED.

3: EXPERIMENT NOT TO BE PROCESSED.

CHAMBER CONDITIONS:

1: MORE THAN 24 HOURS VENTING.

2: DRYING PERFORMED BUT CHAMBER CONDENSATION OBSERVED.

EXPERIMENT STARTS: SUNRISE -	0705
INITIAL CONDITIONS ESTABLISHED: BEFORE SR	0605
EXPERIMENTS ENDS:	1800
RUN QUALITY INDEX:	4.0/10

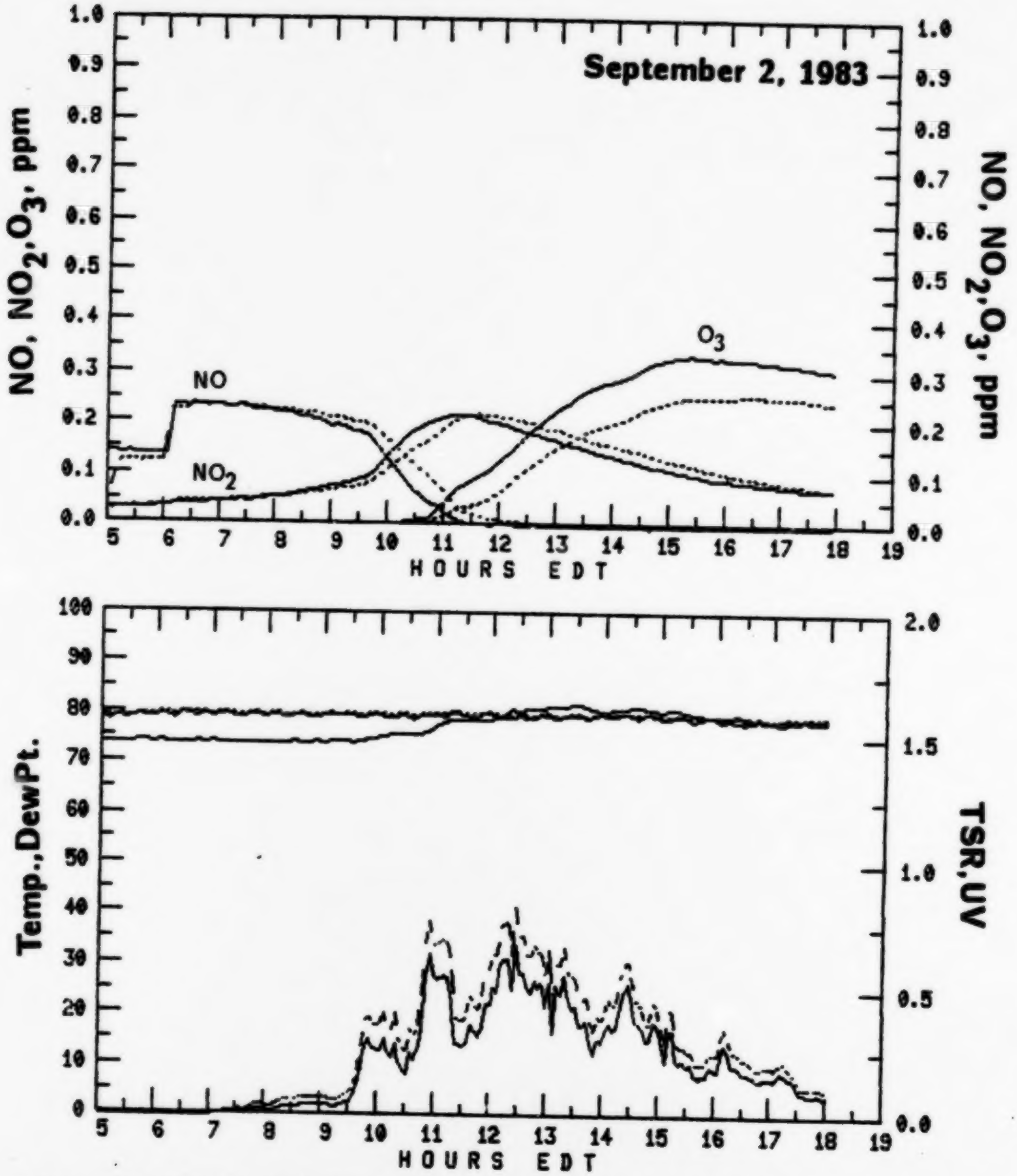


Figure D25. TOP: Synthetic Auto Exhaust, NMHC= 2.39 ppmC, (dashed lines); Dodge Charger, direct injection, NMHC= 3.0 ppmC, (solid lines).
BOTTOM: Chamber air temperature and dew point; ambient total solar and ultraviolet radiation;

September 9, 1983

Synthetic Automobile Exhaust (BLUE) vs Direct Injection from Dodge Charger (RED)

INITIAL CONDITIONS:	BLUE	RED
NO	0.280	0.283
NO2	0.028	0.023
DODGE CHARGER	0.0	2.80
SYNTHETIC EXHAUST NMHC	2.06	0.0
CO	0.3	45.0
	MORN	AFTERNOON
SUNLIGHT AND WEATHER:	7.5/10	8.0/10
TEMPERATURE F:	67.0	97.0

INSTRUMENTS USED:

1: CARLE I GC

2: CARLE II GC

3: CARLE III GC

4: PERKIN ELMER 900 GC

5: BECKMAN 6800 THC/CH4

6: CEA FORMALDEHYDE

7: VARIAN GC

8: DNPH ALDEHYDES (QUALITATIVE)

DATA EXCEPTIONS: ACETALDEHYDE.

SPECIAL PROBLEMS OR CONCERNS:

1: CLOUDY SUN MIDMORNING.

2: CO NOT INJECTED INTO SYNTHETIC MIX TO MATCH CO IN EXHAUST.

CHAMBER CONDITIONS:

1: MORE THAN 24 HOURS VENTING.

2: DRYING PERFORMED; NO CHAMBER CONDENSATION OBSERVED.

EXPERIMENT STARTS: SUNRISE - 0645

INITIAL CONDITIONS ESTABLISHED: BEFORE SR 0555

EXPERIMENTS ENDS: 1800

RUN QUALITY INDEX: 7.0/10

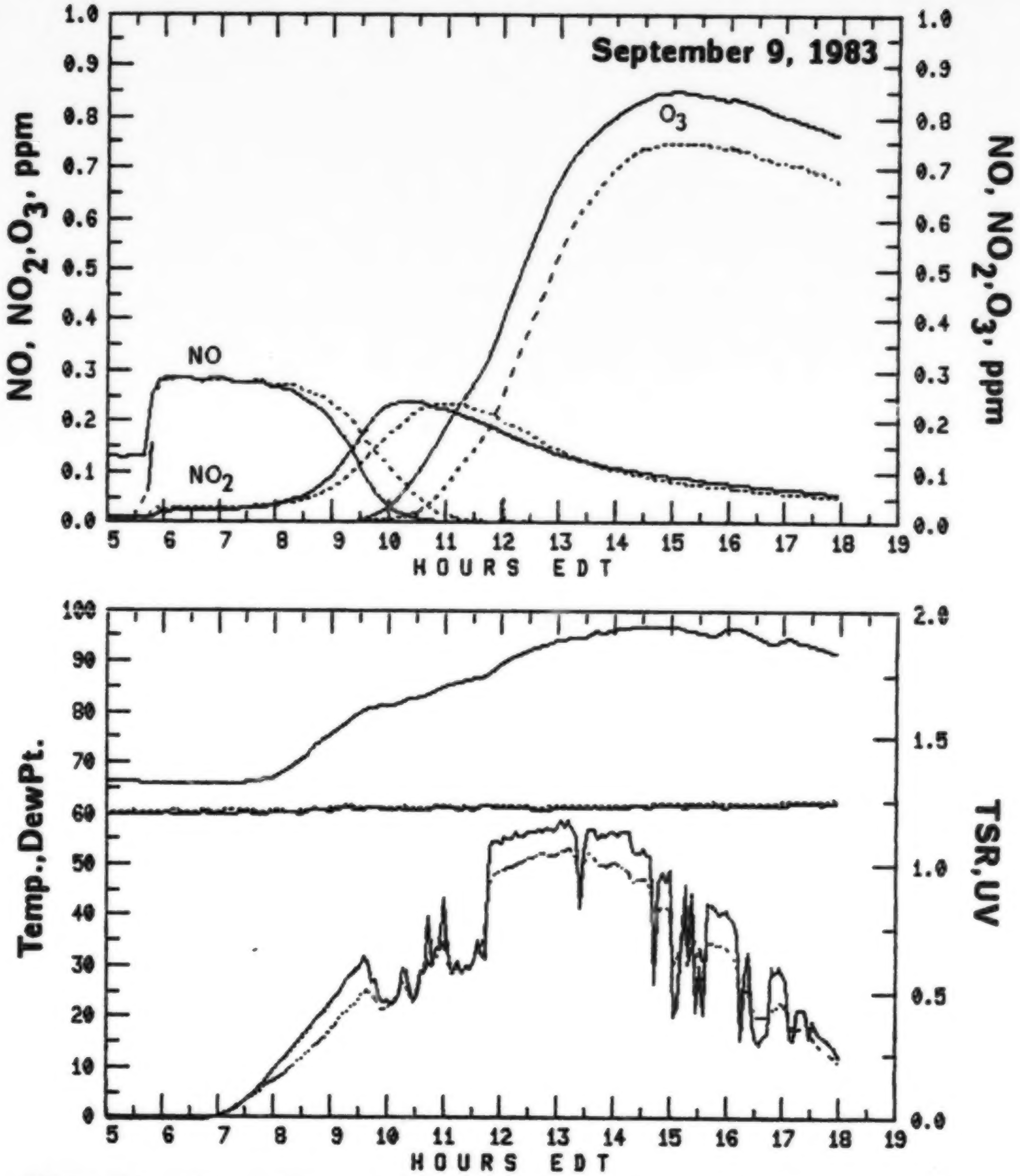


Figure D26. TOP: Synthetic Auto Exhaust, NMHC= 2.55 ppmC, (dashed lines); Dodge Charger, direct injection, NMHC= 2.80 ppmC, (solid lines).
BOTTOM: Chamber air temperature and dew point; ambient total solar and ultraviolet radiation;

September 20, 1983

Synthetic Automobile Exhaust (BLUE) vs Direct Injection from Dodge Charger (RED)

INITIAL CONDITIONS:	BLUE	RED
NO	0.235	0.230
NO2	0.014	0.020
DODGE CHARGER	0.0	2.94
SYNTHETIC EXHAUST NMHC	2.4	0.0
CO	20.3	15.9
	MORN	AFTERNOON
SUNLIGHT AND WEATHER:	3.0/10	2.0/10
TEMPERATURE F:	67.0	89.1

INSTRUMENTS USED:

1: CARLE I GC

2: CARLE II GC

3: CARLE III GC

4: PERKIN ELMER 900 GC

5: BECKMAN 6800 THC/CH4

6: CEA FORMALDEHYDE

7: VARIAN GC

8: DNPH ALDEHYDES (QUALITATIVE)

DATA EXCEPTIONS:

1: PE900 AROMATICS.

2: ACETALDEHYDE.

3: DNPH ALDEHYDES.

SPECIAL PROBLEMS OR CONCERNS:

1: VERY POOR SUN.

2: CONDENSATION OBSERVED IN BOTH CHAMBERS.

3: EXPERIMENT NOT TO BE PROCESSED.

CHAMBER CONDITIONS:

1: MORE THAN 24 HOURS VENTING.

2: DRYING PERFORMED BUT CHAMBER CONDENSATION OBSERVED.

EXPERIMENT STARTS: SUNRISE -	0654
INITIAL CONDITIONS ESTABLISHED: BEFORE SR	0530
EXPERIMENTS ENDS:	1730
RUN QUALITY INDEX:	4.0/10

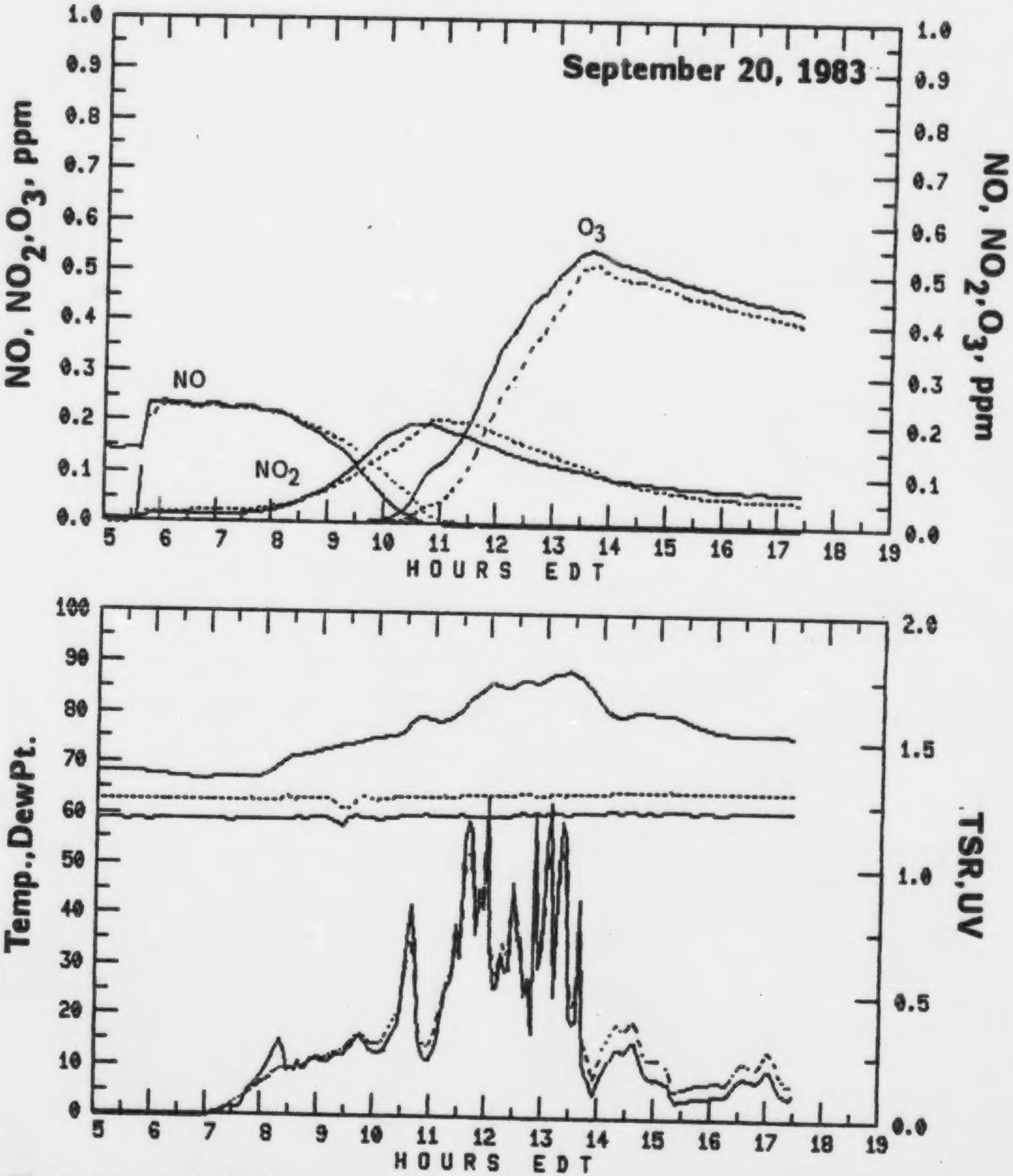


Figure D27. TOP: Synthetic Auto Exhaust, NMHC= 2.40 ppmC, (dashed lines); Dodge Charger, direct injection, NMHC= 2.94 ppmC, (solid lines).
BOTTOM: Chamber air temperature and dew point; ambient total solar and ultraviolet radiation;

October 4, 1983

Synthetic Automobile Exhaust (BLUE) vs Direct Injection from Dodge Charger (RED)

INITIAL CONDITIONS:	BLUE	RED
NO	0.214	0.215
NO2	0.037	0.039
DODGE CHARGER, NMHC	0.0	2.587
SYNTHETIC EXHAUST NMHC	2.190	0.0
ETHYLENE	0.450	
PROPYLENE	0.092	
1-BUTENE	0.055	
TRANS-2-BUTENE	0.038	
N-BUTANE	0.107	
ISOPENTANE	0.152	
2,2,4-TRIMETHYLPENTANE	0.226	
BENZENE	0.127	
TOLUENE	0.512	
M-XYLENE	0.220	
O-XYLENE	0.086	
1,2,4-TRIMETHYLBENZENE	0.124	
FORMALDEHYDE	0.043	
CO	20.3	15.9

	MORN	AFTERNOON
SUNLIGHT AND WEATHER:	9.0/10	7.5/10
TEMPERATURE F:	54.5	90.0

INSTRUMENTS USED:

1: CARLE I GC
2: CARLE II GC
3: CARLE III GC
4: PERKIN ELMER 900 GC
5: BECKMAN 6800 THC/CH4
6: CEA FORMALDEHYDE
7: VARIAN GC

DATA EXCEPTIONS:
1: PE900 AROMATICS (AFTER INITIAL CONDITIONS).
2: ACETALDEHYDE.
3: DNPH ALDEHYDES.

SPECIAL PROBLEMS OR CONCERNS:
1: SOME CONDENSATION OBSERVED IN BOTH CHAMBERS.

CHAMBER CONDITIONS:
1: MORE THAN 24 HOURS VENTING.
2: DRYING PERFORMED BUT SOME CHAMBER CONDENSATION OBSERVED.

EXPERIMENT STARTS: SUNRISE -	0704
INITIAL CONDITIONS ESTABLISHED: BEFORE SR	0615
EXPERIMENTS ENDS:	1706
RUN QUALITY INDEX:	8.8/10

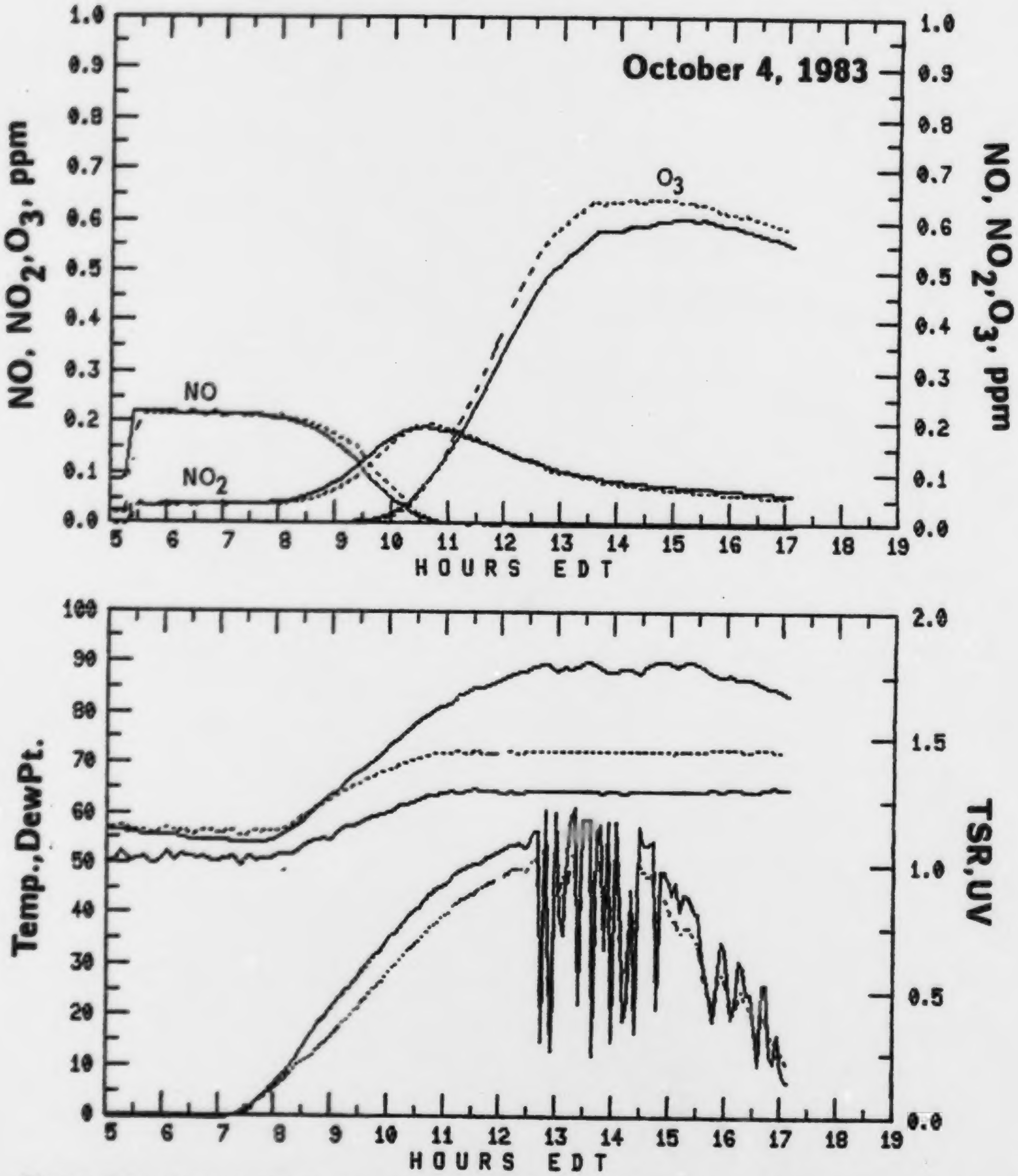


Figure D28. TOP: Synthetic Auto Exhaust, NMHC= 2.19 ppmC, (dashed lines); Dodge Charger, direct injection, NMHC= 2.59 ppmC, (solid lines).
BOTTOM: Chamber air temperature and dew point; ambient total solar and ultraviolet radiation;

Initial Conditions for October 4, 1983

		SYNT			DC/66		
		BLUE			RED		
	Cnum Split *	PPMC	%C	PPMV	RED	%C	PPMV
PARAFFINS							
ethane	2	0.000	0.00	0.000	0.024	0.93	0.012
propane	3	0.000	0.00	0.000	0.015	0.58	0.005
n-butane	4	0.107	4.89	0.027	0.092	3.56	0.023
i-butane	4	0.000	0.00	0.000	0.021	0.81	0.005
i-pentane	5	0.152	6.94	0.030	0.120	4.64	0.024
n-pentane	5	0.000	0.00	0.000	0.063	2.44	0.013
2-me-pentane	6	0.000	0.00	0.000	0.048	1.86	0.008
trime-pentanes	8	0.226	10.32	0.028	0.050	1.93	0.006
octane	8	0.000	0.00	0.000	ND	NA	ND
C6 unk(C1G)	6	0.000	0.00	0.000	0.031	1.20	0.005
Sub-total		0.485	22.15	0.085	0.464	17.94	0.101
OLEFINS							
ethylene	2	0.450	20.55	0.225	0.201	7.77	0.101
propylene	3	0.092	4.20	0.031	0.075	2.90	0.025
1-butene	4	0.055	2.51	0.014	0.016	0.62	0.004
c-2-butene	4	0.000	0.00	0.000	0.007	0.27	0.002
t-2-butene	4	0.038	1.74	0.010	0.004	0.15	0.001
1,3butadiene	4	0.000	0.00	0.000	0.013	0.50	0.003
2-me-1-butene	5		0.00	0.000	0.008	0.29	0.002
2-me-2-butene	5		0.00	0.000	ND	NA	ND
Sub-total		0.635	29.00	0.279	0.324	12.50	0.137

AROMATICS								
benzene	6		0.127	5.80	0.021	0.177	6.84	0.030
toluene	7		0.512	23.38	0.073	0.258	9.97	0.037
mp-xylene	8		0.220	10.05	0.028	0.169	6.53	0.021
et-benzenes	8		0.000	0.00	0.000	0.040	1.55	0.005
pro-benzenes	9		0.000	0.00	0.000	0.065	2.51	0.007
o-xylene	8		0.086	3.93	0.011	0.082	3.17	0.010
135-C3-benzene	9		0.000	0.00	0.000	0.035	1.35	0.004
123-C3-benzene	9		0.000	0.00	0.000	ND	NA	ND
124-C3-benzene	9		0.124	5.66	0.014	0.090	3.48	0.010
dimeet-benzene	10		0.000	0.00	0.000	ND	NA	ND
m-eth-toluene	9		0.000	0.00	0.000	0.075	2.90	0.008
o-eth-toluene	9		0.000	0.00	0.000	ND	NA	ND
styrene	8		0.000	0.00	0.000	0.015	0.58	0.002
napthalene	10		0.000	0.00	0.000	0.090	3.48	0.009
2me-napthalene	11		0.000	0.00	0.000	ND	NA	ND
1me-napthalene	11		0.000	0.00	0.000	ND	NA	ND
others	10	4	0.000	0.00	0.000	ND	NA	ND
Sub-total			1.069	48.81	0.146	1.096	42.37	0.143
ACETYLENE								
acetylene	2		0.000	0.00	0.000	0.209	8.08	0.105
TOTAL MEASURED SPECIES			2.189	99.95	0.511	2.093	80.89	0.486
Unspeciated Carbon			0.001	0.05		0.495	19.11	
FINAL NMHC			2.190			2.587		

```
                                                      |
                                                      |

######################################################|###########################
                                                      |
SUMMARY                                               |
                            PPMC       %C    Car Num |  PPMC       %C     Car Num
                                                      |
     Meas PAR                0.485     22.15      5.68 |  0.464     17.94      4.58
     Est  PAR                0.000      0.00      0.00 |  0.300     11.60      6.37
                          ----------------------------|---------------------------
     TOT  PAR           5    0.485     22.15      5.68 |  0.764     29.53      5.15
                                                      |
                                                      |
     Meas OLE                0.635     29.00      2.28 |  0.324     12.50      2.36
      Est OLE                0.000      0.00      0.00 |  0.095      4.34      3.50
                          ----------------------------|---------------------------
      TOT OLE           5    0.635     29.00      2.28 |  0.419     16.18      2.55
                                                      |
                                                      |
     Meas ARO                1.069     48.81      7.31 |  1.096     42.37      7.66
      Est ARO                0.000      0.00      0.00 |  0.100      4.57     10.75
                          ----------------------------|---------------------------
                        5    1.069     48.81      7.31 |  1.196     46.23      7.85
                                                      |
     Meas ACE                0.000      0.00       ERR |  0.209      8.08      2.00
                          ----------------------------|---------------------------
      TOT ACE                0.000      0.00       ERR |  0.209      8.08      2.00
                                                      |
--------------            ----------------------------|---------------------------
--------------            ----------------------------|---------------------------
      Spec HC                2.189     99.95           |  2.093     80.89
    Unspec HC                0.000      0.00           |  0.495     19.13
                          ------------------          |------------------
     TOT NMHC                2.189     99.95           |  2.588    100.02
```

October 7, 1983

Synthetic Automobile Exhaust (BLUE) vs Synthetic Urban Mix (RED)

INITIAL CONDITIONS:	BLUE	RED
NO	0.305	0.293
NO2	0.040	0.041
SYNTHETIC EXHAUST NMHC	2.685	0.0
UNCMIX	0.0	1.893
COMARO	0.0	0.753
ETHYLENE	0.623	0.222
PROPYLENE	0.125	0.106
1-BUTENE	0.059	0.054
TRANS-2-BUTENE	0.077	0.0
N-BUTANE	0.1255	0.0
ISOPENTANE	0.157	0.320
2,2,4-TRIMETHYLPENTANE	0.290	0.198
BENZENE	0.166	0.0
TOLUENE	0.514	0.174
M-XYLENE	0.224	0.144
O-XYLENE	0.135	0.0
1,2,4-TRIMETHYLBENZENE	0.192	0.199
CIS-2-BUTENE	0.0	0.052
2-METHYL-1-BUTENE	0.0	0.087
2-METHYL-2-BUTENE	0.0	0.053
N-PENTANE	0.0	0.505
2,4-DIMETHYLPENTANE	0.0	0.199
2-METHYLPENTANE	0.0	0.149
N-PROPYLBENZENE	0.0	0.128
SEC-BUTYLBENZE	0.0	0.108
FORMALDEHYDE	0.06	0.0

	MORN	AFTERNOON
SUNLIGHT AND WEATHER:	9.0/10	8.8/10
TEMPERATURE F:	54.5	80.0

INSTRUMENTS USED:
1: CARLE I GC
2: CARLE III GC
3: BECKMAN 6800 THC/CH4
4: CEA FORMALDEHYDE
5: VARIAN GC

DATA EXCEPTIONS:
1: PE900 AROMATICS.
2: ACETALDEHYDE.
3: DNPH ALDEHYDES.

SPECIAL PROBLEMS OR CONCERNS:
1: SOME CONDENSATION OBSERVED IN BOTH CHAMBERS.

CHAMBER CONDITIONS:
1: MORE THAN 6 HOURS VENTING.
2: DRYING PERFORMED BUT SOME CHAMBER CONDENSATION OBSERVED.

EXPERIMENT STARTS: SUNRISE -	0704
INITIAL CONDITIONS ESTABLISHED: BEFORE SR	0600 FOR HC 0645 FOR HCHO
EXPERIMENTS ENDS:	1759
RUN QUALITY INDEX:	8.3/10

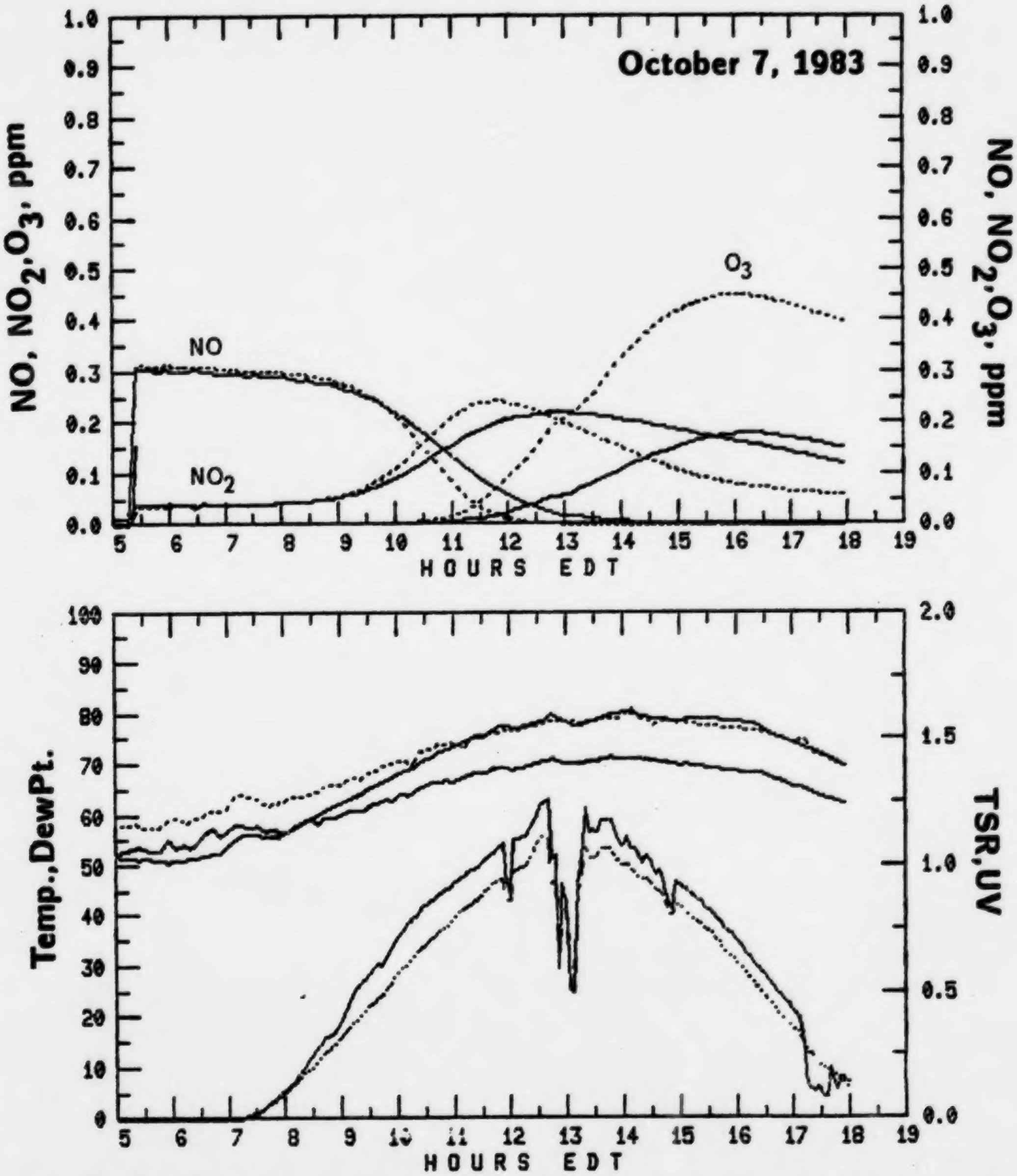


Figure D29. TOP: Synthetic Auto Exhaust, NMHC= 2.69 ppmC, (dashed lines); Synthetic Urban Mixture, NMHC= 2.65 ppmC, (solid lines).
BOTTOM: Chamber air temperature and dew point; ambient total solar and ultraviolet radiation;

Initial Conditions for October 7, 1983

	Cnum	Split *	SYNT Auto BLUE PPMC	%C	PPMV	UNCMIX/COMARO RED RED	%C	PPMV
PARAFFINS								
ethane	2		0.000	0.00	0.000	0.000	0.00	0.000
propane	3		0.000	0.00	0.000	0.000	0.00	0.000
n-butane	4		0.000	0.00	0.000	0.000	0.00	0.000
i-butane	4		0.126	4.89	0.032	0.000	0.00	0.000
i-pentane	5		0.157	6.10	0.031	0.320	12.59	0.064
n-pentane	5		0.000	0.00	0.000	0.505	19.87	0.101
2-me-pentane	6		0.000	0.00	0.000	0.149	5.86	0.025
trime-pentanes	8		0.290	11.26	0.036	0.198	7.79	0.025
dime-pentane	7		0.000	0.00	0.000	0.199	7.83	0.028
C6 unk(C1G)	6		0.000	0.00	0.000	0.000	0.00	0.000
Sub-total			0.573	22.25	0.099	1.371	53.96	0.243
OLEFINS								
ethylene	2		0.623	24.19	0.312	0.222	8.74	0.111
propylene	3		0.125	4.85	0.042	0.106	4.17	0.035
1-butene	4		0.056	2.17	0.014	0.054	2.13	0.014
c-2-butene	4		0.000	0.00	0.000	0.052	2.05	0.013
t-2-butene	4		0.077	2.99	0.019	0.000	0.00	0.000
1,3butadiene	4		0.000	0.00	0.000	0.000	0.00	0.000
2-me-1-butene	5			0.00	0.000	0.087	3.42	0.017
2-me-2-butene	5			0.00	0.000	0.053	2.09	0.011
Sub-total			0.881	34.21	0.386	0.574	22.59	0.201

AROMATICS								
benzene	6		0.166	6.45	0.028	0.000	0.00	0.000
toluene	7		0.514	19.96	0.073	0.174	6.85	0.025
mp-xylene	8		0.224	8.70	0.028	0.144	5.67	0.018
butyl-benzene	8		0.000	0.00	0.000	0.108	4.25	0.014
pro-benzenes	9		0.000	0.00	0.000	0.128	5.04	0.014
o-xylene	8		0.135	5.24	0.017	0.000	0.00	0.000
135-C3-benzene	9		0.000	0.00	0.000	0.000	0.00	0.000
123-C3-benzene	9		0.000	0.00	0.000	0.000	0.00	0.000
124-C3-benzene	9		0.192	7.46	0.021	0.199	7.83	0.022
dimeet-benzene	10		0.000	0.00	0.000	0.000	0.00	0.000
m-eth-toluene	9		0.000	0.00	0.000	0.000	0.00	0.000
o-eth-toluene	9		0.000	0.00	0.000	0.000	0.00	0.000
styrene	8		0.000	0.00	0.000	0.000	0.00	0.000
napthalene	10		0.000	0.00	0.000	0.000	0.00	0.000
2me-napthalene	11		0.000	0.00	0.000	0.000	0.00	0.000
1me-mapthalene	11		0.000	0.00	0.000	0.000	0.00	0.000
others	10	4	0.000	0.00	0.000	0.000	0.00	0.000
Sub-total			1.231	47.81	0.167	0.753	29.63	0.093
ACETYLENE								
acetylene	2		0.000	0.00	0.000	0.000	0.00	0.000
TOTAL MEASURED SPECIES			2.685	104.27	0.653	2.698	106.18	0.537
Unspeciated Carbon			-0.110	-4.27		-0.157	-6.18	
FINAL NMHC			2.575			2.541		

```
                                                   |
                                                   |
###################################################|##########################
                                                   |
SUMMARY                                            |
                          PPMC      %C    Car Num  |  PPMC      %C    Car Num
                                                   |
     Meas PAR            0.573    22.25     5.78   |  1.371    53.96     5.64
     Est  PAR            0.000     0.00     0.00   |  0.000     0.00     0.00
                       ----------------------------|---------------------------
     TOT  PAR        5   0.573    22.25     5.78   |  1.371    53.96     5.64
                                                   |
                                                   |
     Meas OLE            0.881    34.21     2.28   |  0.574    22.59     2.86
      Est OLE            0.000     0.00     0.00   |  0.000     0.00     0.00
                       ----------------------------|---------------------------
      TOT OLE        5   0.881    34.21     2.28   |  0.574    22.59     2.86
                                                   |
                                                   |
     Meas ARO            1.231    47.81     7.36   |  0.753    29.63     8.12
      Est ARO            0.000     0.00     0.00   |  0.000     0.00     0.00
                       ----------------------------|---------------------------
                     5   1.231    47.81     7.36   |  0.753    29.63     8.12
                                                   |
     Meas ACE            0.000     0.00     0.00   |  0.000     0.00     0.00
                       ----------------------------|---------------------------
      TOT ACE            0.000     0.00     0.00   |  0.000     0.00     0.00
                                                   |
--------------         ----------------------------|---------------------------
--------------         ----------------------------|---------------------------
      Spec HC            2.685   104.27            |  2.698   106.18
    Unspec HC            0.000     0.00            |  0.000     0.00
                       -------------------         |-------------------
     TOT NMHC            2.685   104.27            |  2.698   106.18
```

October 19, 1983

Matched Direct Injections from Plymouth Volare (BLUE) and Dodge Charger (RED)

INITIAL CONDITIONS:	BLUE	RED
NO	0.762	0.756
NO2	0.074	0.078
VOLARE	0.35	0.0
CHARGER	0.0	0.35
CO	1.19	3.05

	MORN	AFTERNOON
SUNLIGHT AND WEATHER:	7/10	6/10
TEMPERATURE F:	49	78

INSTRUMENTS USED:

1: CARLE I GC
2: CARLE II GC
3: CARLE III GC
4: PERKIN ELMER 900 GC
5: BECKMAN 6800 THC/CH4
6: CEA FORMALDEHYDE
7: VARIAN GC
8: DNPH ALDEHYDES (QUALITATIVE)

DATA EXCEPTIONS:

1: ACETALDEHYDE.
2: LOST DVM DATA FILE: TEMPERATURE. NOX, O3, TSR AND UV PICKED FROM STRIPCHART.

SPECIAL PROBLEMS OR CONCERNS:

1: VERY COOL MORNING AND CONDENSATION OBSERVED.

CHAMBER CONDITIONS:

1: MORE THAN 24 HOURS OF VENTING BEFORE RUN.
2: DRYING PERFORMED; CONDENSATION OBSERVED.

EXPERIMENT STARTS:	0652
INITIAL CONDITIONS ESTABLISHED:	0640
EXPERIMENTS ENDS:	1720
RUN QUALITY INDEX:	7/10

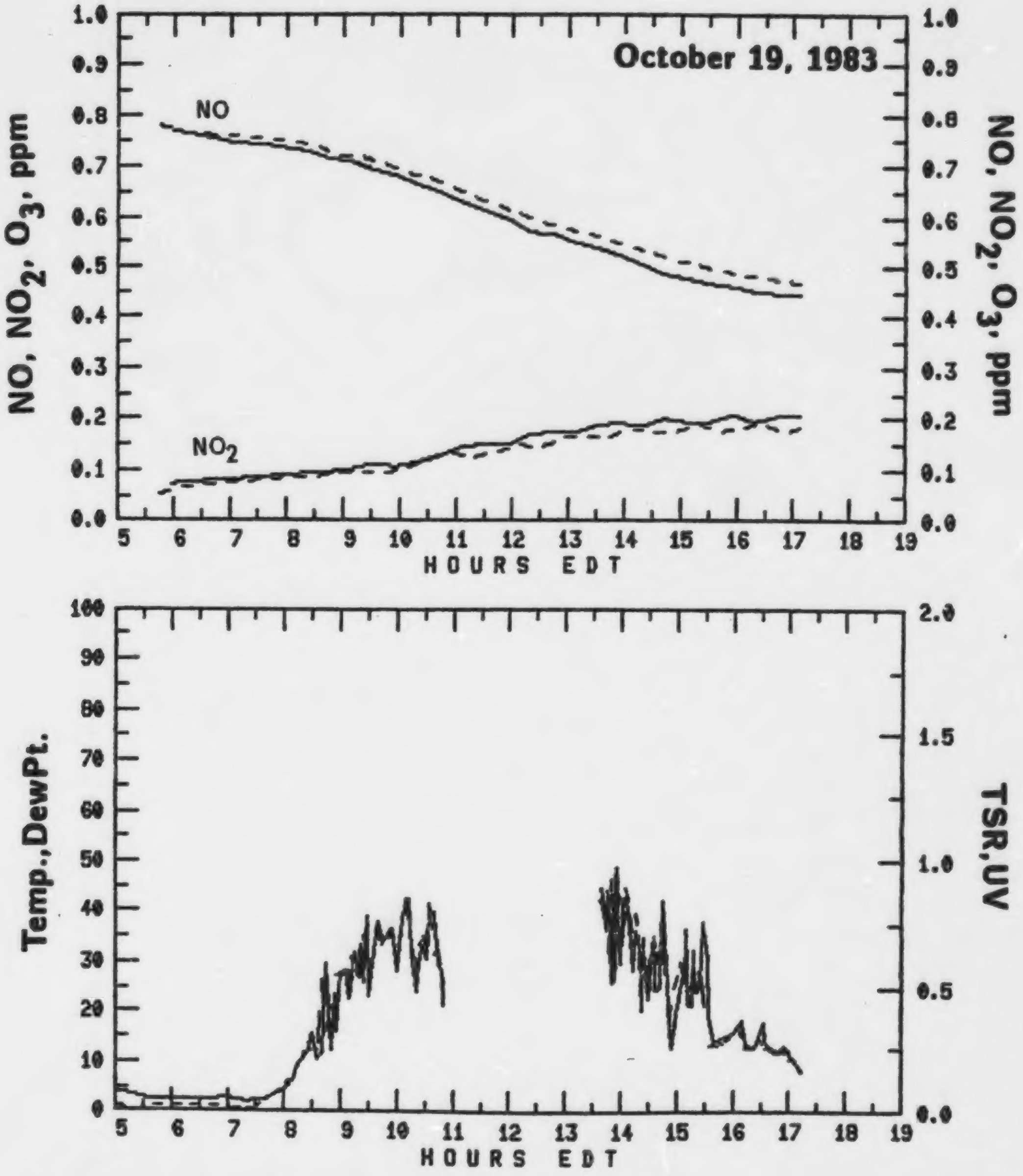


Figure D30. TOP: Plymouth Volare, direct injection, NMHC= 0.35 ppmC, (dashed lines); Dodge Charger, direct injection, NMHC= 0.35 ppmC, (solid lines).
BOTTOM: Chamber air temperature and dew point; ambient total solar and ultraviolet radiation;

October 28, 1983

Matched Direct Injections from Dodge Charger (BLUE) and Plymouth Volare (RED)

INITIAL CONDITIONS:	BLUE	RED
NO	0.233	0.250
NO2	0.025	0.029
VOLARE	0.0	2.403
CHARGER	2.366	0.00
CO		

	MORN	AFTERNOON
SUNLIGHT AND WEATHER:	8.5/10	10/10
TEMPERATURE F:	35	75

INSTRUMENTS USED:

1: CARLE I GC
2: CARLE II GC
3: CARLE III GC
4: PERKIN ELMER 900 GC
5: BECKMAN 6800 THC/CH4
6: CEA FORMALDEHYDE
7: VARIAN GC
8: DNPH ALDEHYDES (QUALITATIVE)
9: SIGMA 2

DATA EXCEPTIONS:

1: ACETALDEHYDE.
2: DNPH ALDEHYDES.
3: INITIAL DEW POINT DATA UNTIL 10AM

SPECIAL PROBLEMS OR CONCERNS:

1: VERY COOL MORNING; FROST OBSERVED.
2: OVERINJECTED WITH PLYMOUTH VOLARE INITIALLY. HAD TO VENT DOWN.
3: CRYO SAMPLES TAKEN FOR GC/MS ANALYSIS.
4: NEW SIGMA 2 GC USED FOR MORNING ANALYSIS OF HC.

CHAMBER CONDITIONS:
1: MORE THAN 48 HOURS OF VENTING BEFORE RUN.
2: DRYING PERFORMED; FROST OBSERVED.

EXPERIMENT STARTS: 0725
INITIAL CONDITIONS ESTABLISHED: 0625
EXPERIMENTS ENDS: 1630

RUN QUALITY INDEX: 8/10

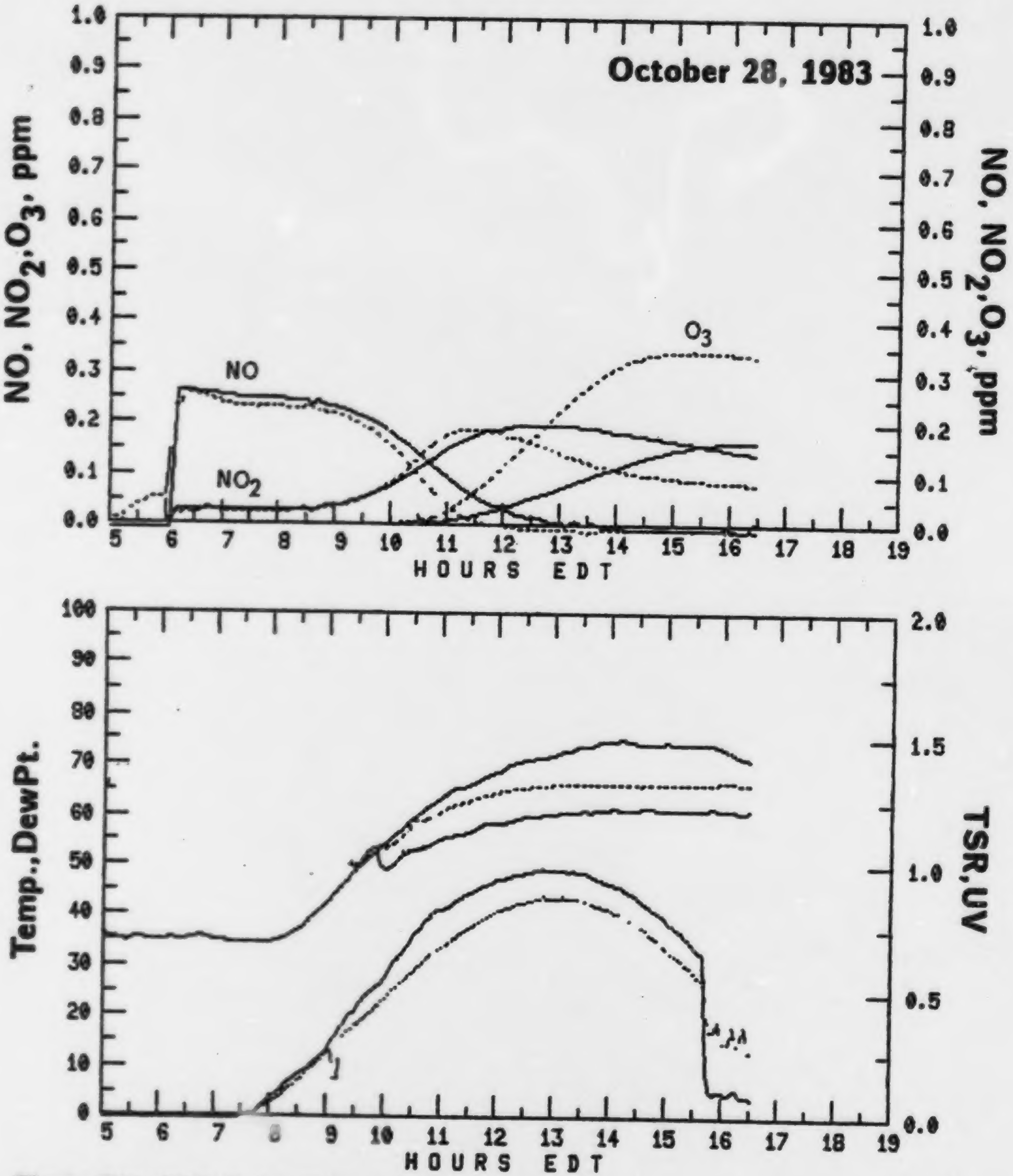


Figure D31. TOP: Dodge Charger, direct injection, NMHC= 2.2 ppmC, (dashed lines); Plymouth Volare, direct injection, NMHC= 2.4 ppmC, (solid lines).
BOTTOM: Chamber air temperature and dew point; ambient total solar and ultraviolet radiation;

November 2, 1983

Matched Direct Injections from Dodge Charger (BLUE) and Plymouth Volare (RED)

INITIAL CONDITIONS:	BLUE	RED
NO	0.297	0.297
NO2	0.024	0.019
VOLARE	0.0	1.56
CHARGER	1.50	0.00
CO	13.5	22.0

	MORN	AFTERNOON
SUNLIGHT AND WEATHER (DAY 1):	7/10	9/10
SUNLIGHT AND WEATHER (DAY 2):	3/10	6.5/10
TEMPERATURE F (DAY1):	48.8	70.9
TEMPERATURE F (DAY2):	50.2	70

INSTRUMENTS USED:

1: CARLE I GC
2: CARLE II GC
3: CARLE III GC
4: PERKIN ELMER 900 GC
5: BECKMAN 6800 THC/CH4
6: CEA FORMALDEHYDE
7: DNPH ALDEHYDES (QUALITATIVE)
8: SIGMA 2

DATA EXCEPTIONS:

1: ACETALDEHYDE.
2: DNPH ALDEHYDES.

SPECIAL PROBLEMS OR CONCERNS:

1: CONDENSATION OBSERVED.
2: CRYO SAMPLES TAKEN FOR GC/MS ANALYSIS.
3: NEW SIGMA 2 GC USED FOR MORNING ANALYSIS OF HC.

CHAMBER CONDITIONS:

1: MORE THAN 100 HOURS OF VENTING BEFORE RUN.
2: NO DRYING PERFORMED; CONDENSATION OBSERVED.

EXPERIMENT STARTS: (SUNRISE)	0730
INITIAL CONDITIONS ESTABLISHED:	0627
EXPERIMENTS ENDS:	1800 (NOV 3)
RUN QUALITY INDEX:	7/10

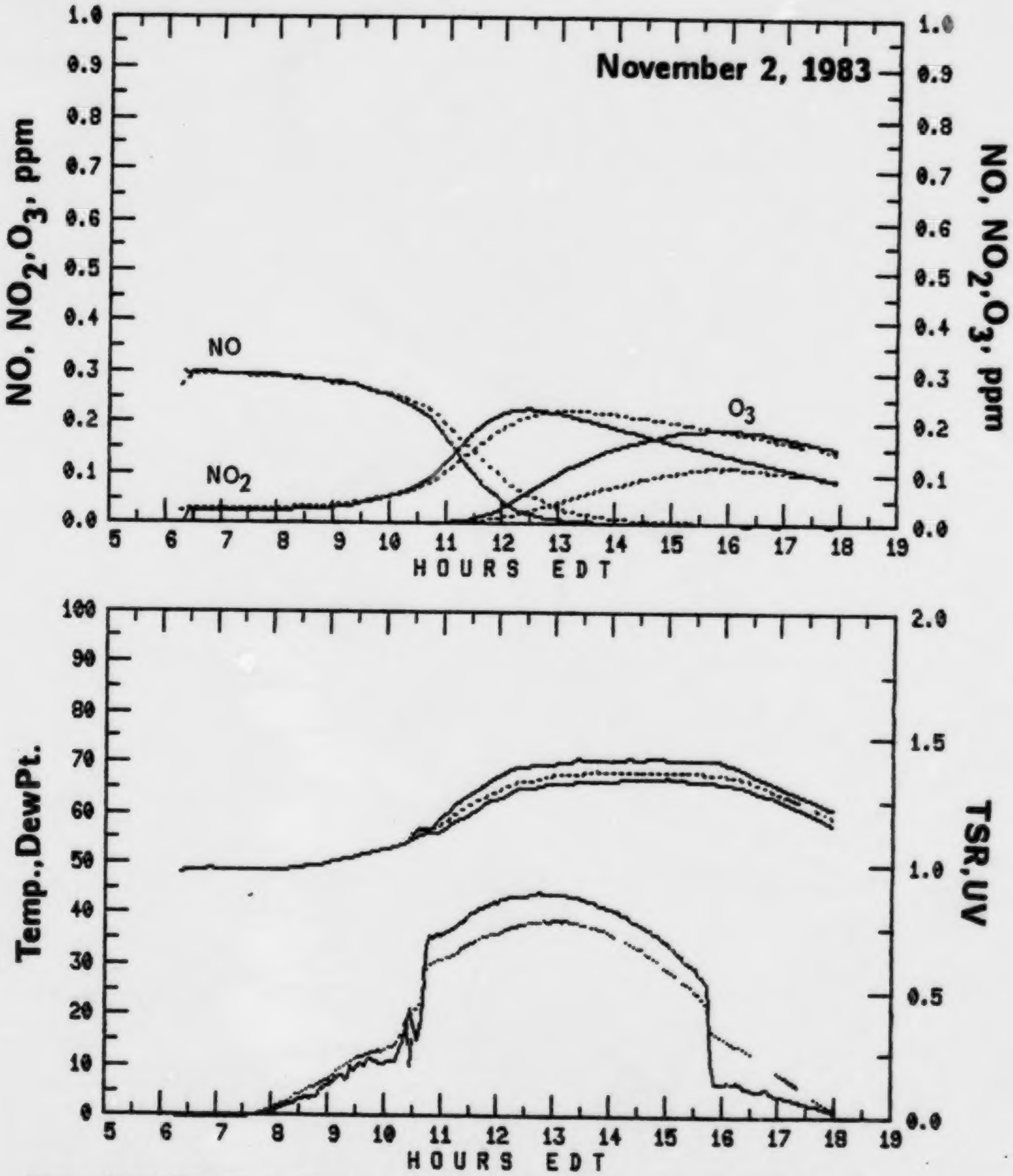


Figure D32. TOP: Dodge Charger, direct injection, NMHC= 1.50 ppmC, (dashed lines); Plymouth Volare, direct injection, NMHC= 1.55 ppmC, (solid lines).
BOTTOM: Chamber air temperature and dew point; ambient total solar and ultraviolet radiation;

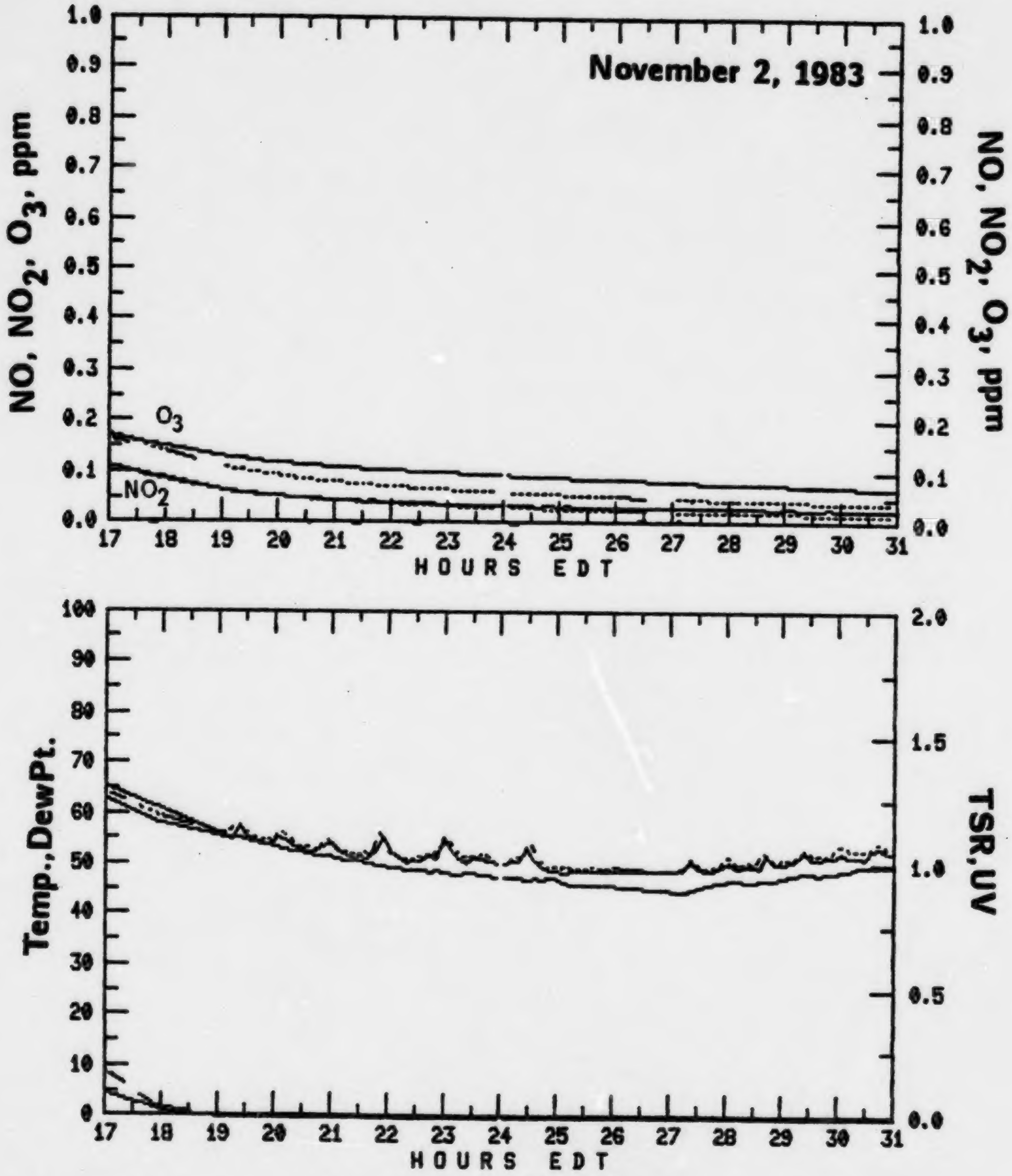


Figure D33. TOP: Continuation (Overnight): Dodge Charger, direct injection, NMHC= 1.50 ppmC, (dashed lines); Plymouth Volare, direct injection, NMHC= 1.55 ppmC, (solid lines). BOTTOM: Chamber air temperature and dew point; ambient total solar and ultraviolet radiation;

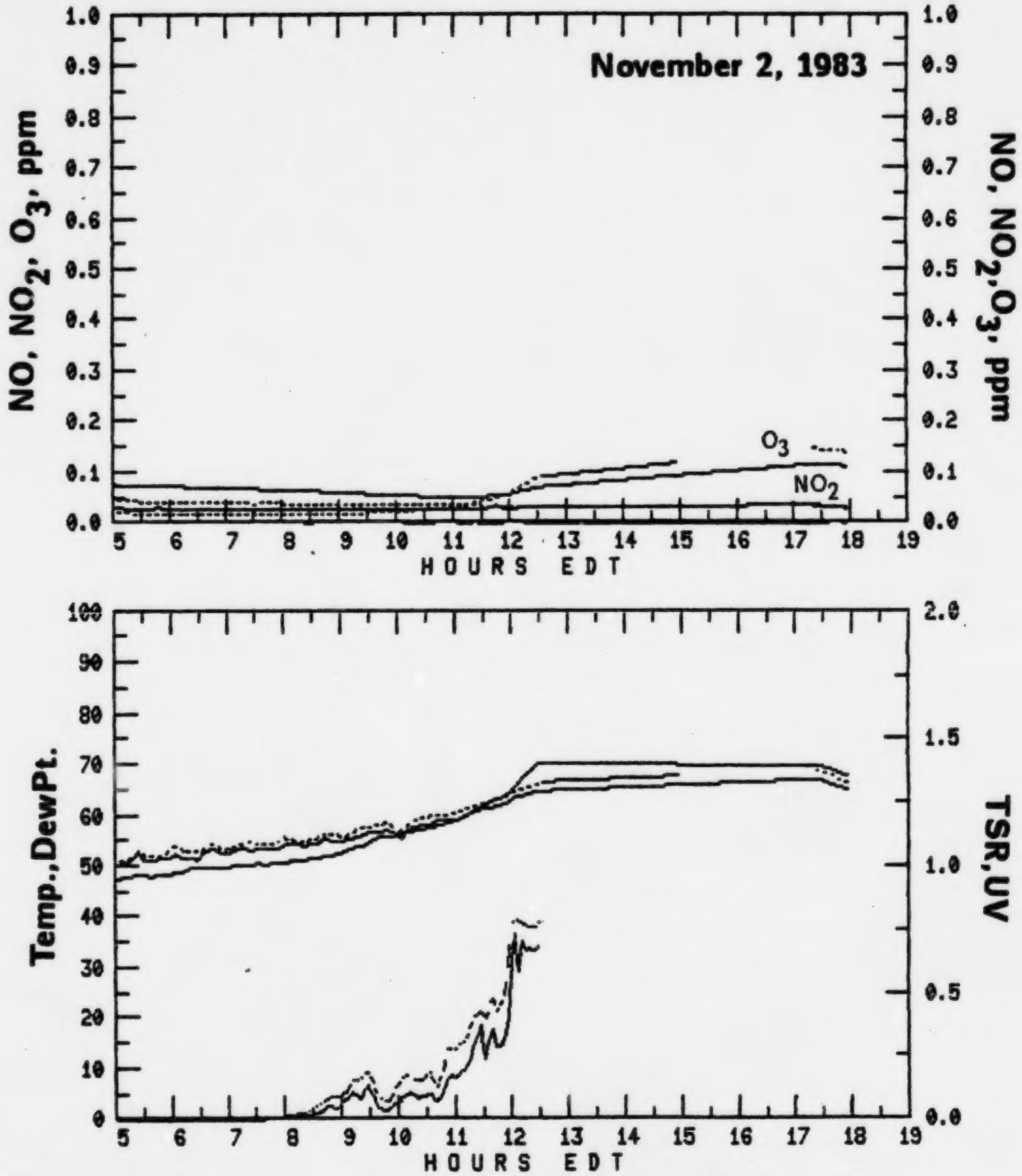


Figure D34. TOP: Continuation (Second Day): Dodge Charger, direct injection, NMHC= 1.50 ppmC, (dashed lines); Plymouth Volare, direct injection, NMHC= 1.55 ppmC, (solid lines). BOTTOM: Chamber air temperature and dew point; ambient total solar and ultraviolet radiation;

6

Discussion

Experimental Findings

The purpose of this section is to describe the major findings from the seven general types of experiments performed. The seven types were:

- matched direct injections from one car into both chamber sides;
- matched injection from one car into both chamber sides, one side directly from the car and the other side from a simultaneous cryocondenser sample;
- matched direct injections from one car into both sides of chamber, different gasolines (regular vs. premium grade) used on the two sides;
- matched direct injections from different cars in each side, same gasoline used in both cars;
- different HC injections from one car in both sides with NO_x balanced; these were EKMA-type runs;
- synthetic HC mixture injected in one side and one car's exhaust injected into the other side;
- matched direct injection from one car and then toluene added to one side and m-xylene added to other side; this was an aromatic substitution into exhaust.

Matched Direct Injections Experiments

The purpose of these experiments was to demonstrate that matched initial concentrations could be injected into the two chamber halves, and that the chambers produced matched results under these conditions. In addition these experiments provided a baseline to compare with other experiments.

Example Run: July 1, 1982

In the July 1, 1982 experiment, the 1972 Dodge Charger and the oscillating valve injection system were used to inject exhaust directly into both chambers. Figure 27 illustrates the principle results. The concentration-time profiles for the two sides of the chamber are shown in the figures as solid and dashed lines. In addition, for GC data, the symbols are filled on the solid lines and are open on the dashed lines.

The first plot shows NO, NO_2, and O_3 for both chamber sides. The chemiluminescent NO_x analyzer responds 100% to PAN but not to nitric acid. The second data plot for each day shows the Beckman 6800 total hydrocarbon analyzer response (BHC) which is presented as percent of full scale rather than as a concentration because of problems in NMHC response for this type instrument. The response is the same for both sides of the chamber, however, and thus the instrument is suitable for showing the relative match in total hydrocarbon. Carbon monoxide (CO) from the same instrument is also shown on this plot. Formaldehyde, determined by an automated reverse West-Gaeke method, is also shown for both sides. In the third plot, time profiles of selected hydrocarbons are shown for both sides. The last plot for each day shows the total solar radiation (TSR), the ultraviolet radiation (UVR) and the chamber temperature. The sudden, sharp changes in TSR were caused by clouds.

In this experiment, the goal of a matched injection system was closely achieved for NMHC (2%), and for CO (2.6%); NO_x, however, was only matched to about 5%. The injection can be seen in Figure 27 as the rise in NO between 0500 and 0530 EDT. The slight mismatch in NO is also evident. In Figure 27, the BHC data and CO data show a very close match. Similarly, the detailed hydrocarbon data show a good match on an individual compound basis. Because of the slight mismatch in the NO, the HC-to-NO_x ratio was 10.3 for the solid side and 11.1 for the dashed side. With less NO, the dashed system reached NO-NO_2 crossover faster (approximately 12 minutes) because the oxidation rates were essentially the same (the two NO lines are congruent). Consequently the dashed system reached NO_2 maximum faster and started to produce ozone faster. Ultimately, the slight initial NO difference of 5% led to 7% more ozone formation.

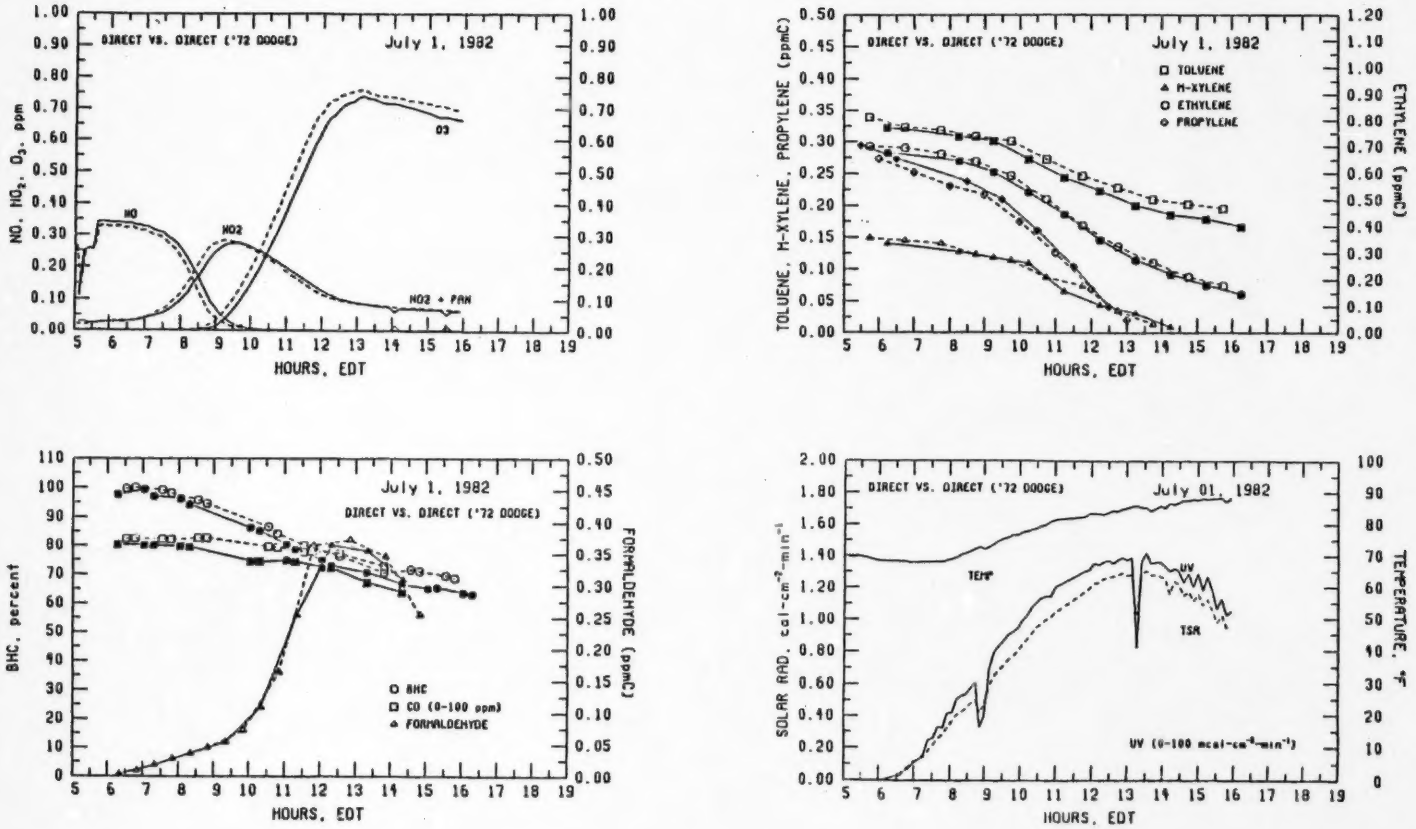


Figure 27. An example of a matched direct injection from the 1972 Dodge Charger. TOP LEFT: NO_x and O_3 data; BOTTOM LEFT: relative NMHC, CO, and formaldehyde data; TOP RIGHT: selected HC species; BOTTOM RIGHT: chamber temperature, total solar and ultraviolet radiation.

Direct/Cryocondenser Injection Experiments

The purpose of these experiments was to demonstrate that automobile exhaust could be sampled and transported, by use of the cryocondenser, without major modification of its reactivity. The tests involved the matched injection of exhaust from one car at the site, one side of the chamber receiving direct exhaust from the tail pipe and the other receiving re-evaporated exhaust from the cryocondenser. The dual glass capillary injection system was used to perform the direct injection into one side. The cryocondenser was used to simultaneously collect exhaust. After the direct injection had finished, the cryocondenser was removed from the LN_2 and connected directly to a manifold into the other chamber side and its contents injected.

Example Run: Sept. 17, 1982

Data for this run are shown in Figure 28; the format is the same as in Figure 27.

In this run, the goal of a matched injection was missed by 11% in NMHC with the cryocondenser side having 0.2 ppmC more NMHC. The NO_x was balanced to within 0.5% . The HC-to-NO_x ratio was 14 on the direct side and 15 on the cryocondenser side. The discrepancy in the NMHC is shown clearly in the BHC and CO data and in the individual HCs shown in Figure 28 . The sunlight was of medium quality on this day with significant cloud cover between 12 and 1300 EDT which affected the ozone formation rate. The cryocondenser side (dashed lines) with 11% more NMHC produced 13% more ozone. The rates and time-to-events of the sides, however, were essentially identical. This result is consistent with previous outdoor chamber results with simple synthetic mixtures.

Aug. 7, 1982 Experiment

Data for this run are shown in Figure 29.

This experiment was performed in a manner similar to that of Sept. 17, 1982 except that less material was injected. Thus a low NMHC concentration was achieved at a HC-to-NO_x ratio of about 3.4. The same injection procedure given above was followed for the cryocondenser.

The rates and time-to-events of the sides were very similar. The amount of formaldehyde produced was well matched. The initial conditions reported suggested that the two sides were well matched. The HC values, however, were very low and

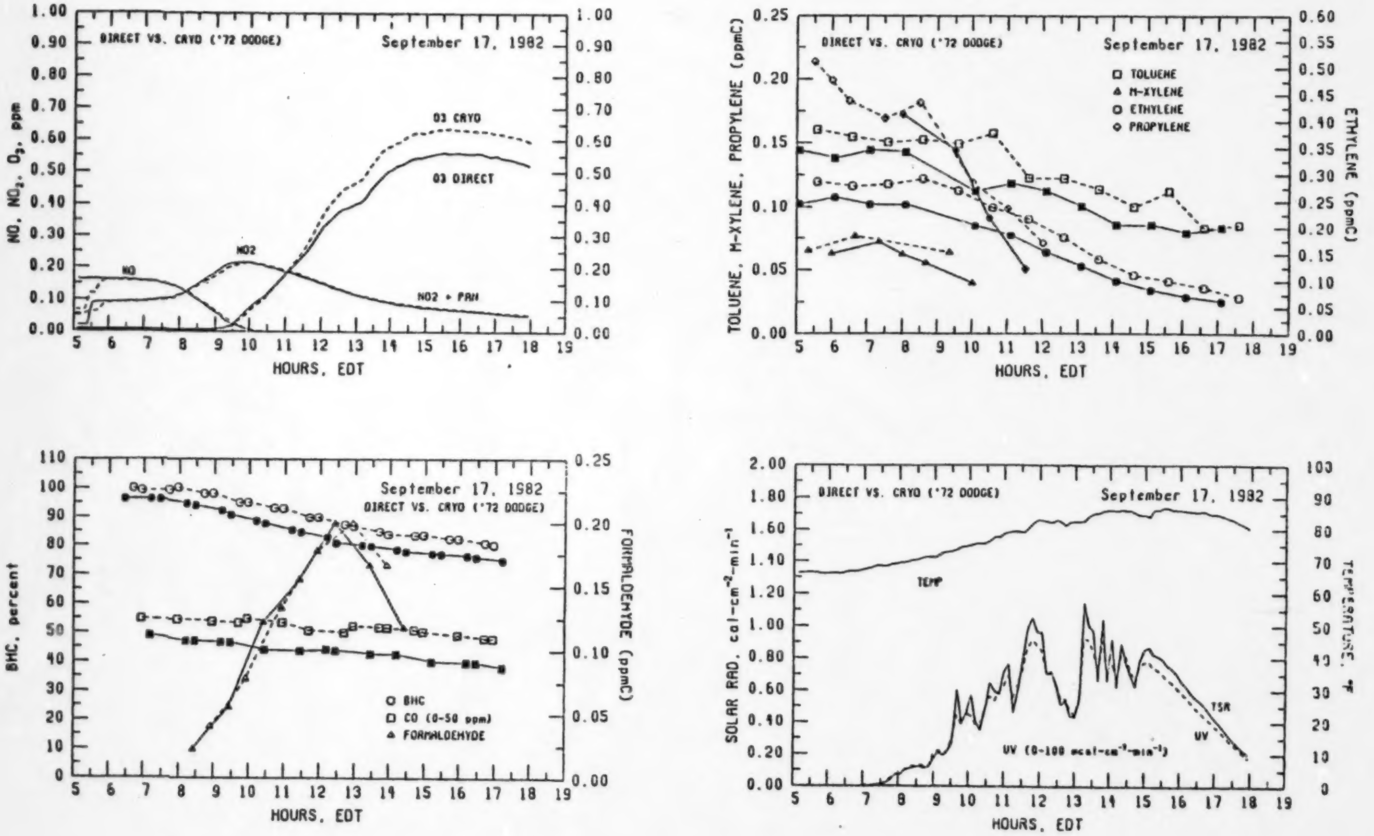


Figure 28. An example of a direct (solid lines) vs. cryocondenser (dashed lines) injection from the 1972 Dodge Charger. TOP LEFT: NO_x and O_3 data; BOTTOM LEFT: relative NMHC, CO, and formaldehyde data; TOP RIGHT: selected HC species; BOTTOM RIGHT: chamber temperature, total solar and ultraviolet radiation.

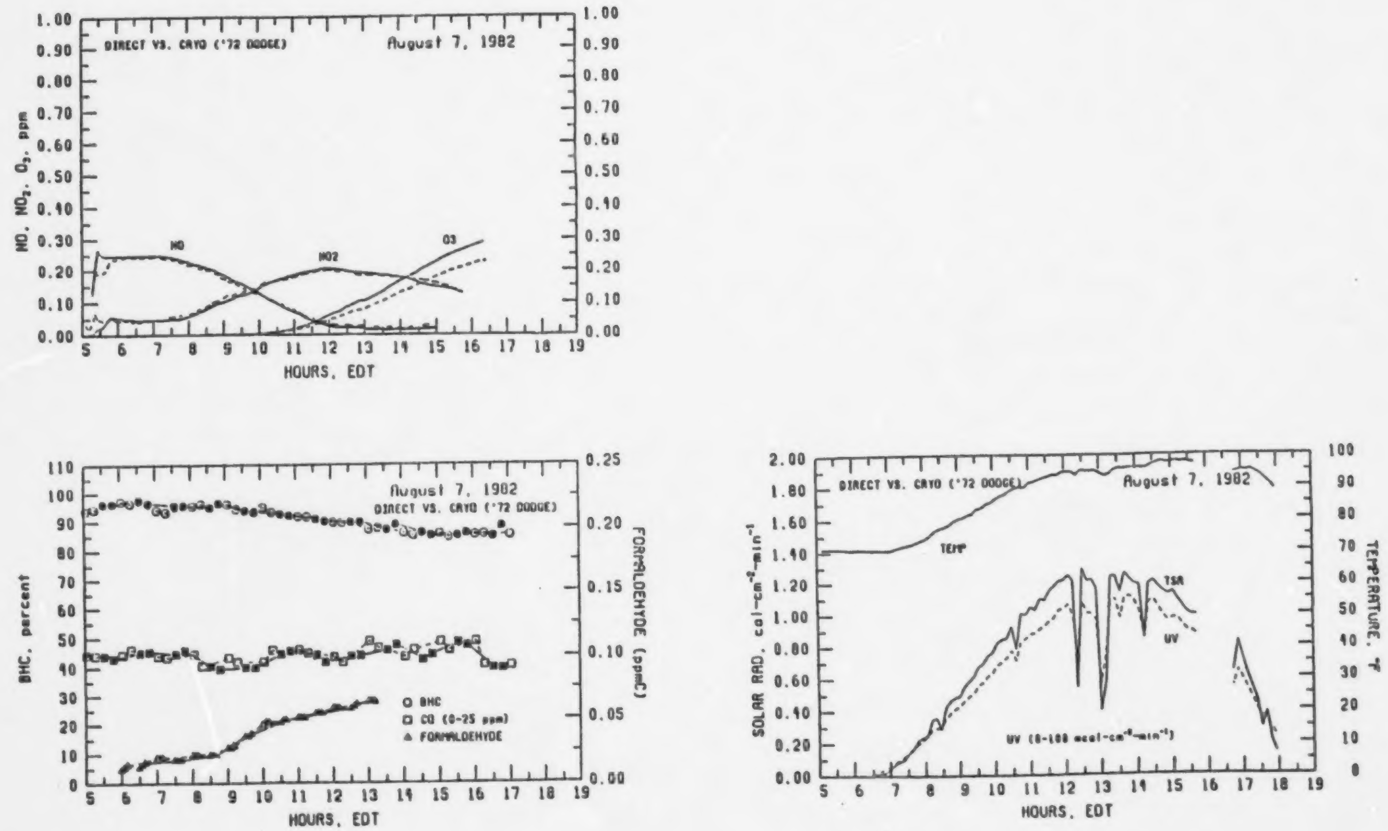


Figure 29. An example of a direct (solid lines) vs. cryocondenser (dashed lines) injection from the 1972 Dodge Charger. TOP LEFT: NO_x and O_3 data; BOTTOM LEFT: relative NMHC, CO, and formaldehyde data; BOTTOM RIGHT: chamber temperature, total solar and ultraviolet radiation.

the measurement of the total NMHC on the two sides was dependent upon differences as small as 0.5 mm pen displacement. The initial values could be interpreted to slightly favor the direct-injection side and this side did produce more ozone than the cryocondenser injected side. Previous outdoor chamber results suggest that extremely carefully matched initial conditions are required to produce exactly the same ozone at HC-to-NO_x ratios as low as in this case.

Same Car/Different Gasoline Experiments

The purpose of these type experiments was to demonstrate the effect that gasoline composition had on reactivity. Only the 1972 Dodge Charger was modified to allow a switch in gasoline after it was started.

Example Runs: July 15, 1983, July 28, 1983

The data plots for these experiments were shown on pages 169 and 179.

The 1972 Dodge Charger using with Phillips 66 non-leaded regular gasoline was used to inject into the BLUE chamber and then the car was switched to Amoco non-leaded premium gasoline and used to inject into the RED chamber. Table 22 summarizes the initial conditions in these runs.

Table 22. Same Car/ Different Gasolines

	July 15		July 28	
Gas	Reg.	Prem	Reg.	Prem
NMHC	2.25	2.19	2.52	2.50
CO	12.37	2.91	1.44	10.8
NO	0.307	0.314	0.255	0.256
NO_2	0.045	0.045	0.036	0.038
O_3	0.922	0.864	0.730	0.770

In both cases, the overall reactivities were similar. In the July 15 experiment, the side with the regular gas was more reactive and in the July 28 experiment the side with the premium gas was more reactive. Note, however, that there was a significant difference in the initial CO concentrations on the two sides in both runs and that in each experiment, the side with the higher CO always made the higest O_3.

Different Cars, Same Gasoline Experiments

The purpose of these experiments was to demonstrate the relative reactivities of un-controlled and controlled cars when other factors were the same.

Example Runs: July 2, 1983; July 8, 1983

Table 23 summarizes the initial conditions for these runs; the data plots are on pages 162 and 167.

Both cars were operated with Phillips 66 non-leaded regular gasoline. The 1972 Dodge Charger was used to inject one side of the chamber and the 1979 Plymouth Volare was used to inject the other side of the chamber in these experiments.

Table 23. Different Cars/ Same Gasoline

	July 2		July 8	
Car	Volare	Dodge	Volare	Dodge
NMHC	1.700	1.64	1.69	1.73
CO	38.6	10.6	28.4	13.4
NO	0.162	0.164	0.306	0.308
NO_2	0.022	0.014	0.062	0.064
O_3	0.697	0.595	0.879	0.756

Note that both of these runs had the same initial NMHC but different initial NO_x. Even though the HC-to-NO_x ratio was different in these runs, the controlled car (the Volare) produced 16-17% more O_3 than the uncontrolled car (the Charger) in both experiments.

EKMA type Experiments

The purpose of these experiments was to provide a test of a model's ability to correctly predict the same $\Delta O_3/\Delta HC$ as shown by chamber conditions. That is, to see if the models would predict the same % reduction in O_3 for a given % reduction in NMHC as was exhibited by the chamber.

Example Runs: June 29, 1983; Aug. 11, 1983

Table 24 summarizes the initial conditions for these runs; the data plots are on pages 160 and 181.

In these experiments, one car was used to inject both sides of the chamber. The injection was 3 seconds on one side and 1 second on the other side for about 45 minutes. After the exhaust injection was finished, the side that had received the low injection received an additional injection of NO_x from tanks to balance the NO_x on both sides. This created a situation that would have resulted if there had been a 66% reduction in NMHC from the car.

Table 24. EKMA-Type Experiments

	June 29		Aug. 11	
NMHC	0.80	2.50	0.678	2.15
CO	4.1	13.8	17.1	57.3
NO	0.115	0.105	0.185	0.185
NO_2	0.040	0.035	0.043	0.038
O_3	0.300	0.460	0.601	0.850

Note that the June 29 experiment was performed with the Dodge Charger and the Aug. 11 experiment was performed with the Plymouth Volare. The "uncontrolled" side of June 29 had an initial NMHC-to-NO_x ratio of 18, whereas on Aug. 11, this side had an initial NMHC-to-NO_x ratio of 10. Even though the ratio was different, both runs predicted about the same benefit in O_3 reduction as a result of NMHC reduction(*i.e.* 36% reduction in O_3 for a 68% reduction in NMHC vs. 30% reduction in O_3 for a 63% reduction in NMHC).

Synthetic vs. Real Exhaust Experiments

The purpose of these experiments was to demonstrate that a 10–15 component HC mixture would exhibit the same general reactivity as real automobile exhaust. The synthetic mixture was described on pages 41–42 in Chapter 4, Methods.

Table 25 summarizes the initial conditions for these four experiments; the data plots are on pages 186, 188, 190, and 193.

In performing these experiments, the injection from the car was performed first. Then the site operators used the Carle GCs to determine the initial NMHC and to estimate the fraction of the exhaust that was acetylene (the synthetic mixture did not contain acetylene which was considered un-reactive). Once the NMHC, non-acetylene HC concentration was known, the synthetic mixture was injected in three parts: the liquid components from a premixed blend; the gaseous components from tanks; and formaldehyde by subliming paraformaldehyde. Only after analyzing the outcome from the first two experiments did we remember to add CO to the synthetic side.

Table 25. Synthetic vs. Real Exhaust

	Sept. 2		Sept 9		Sept. 20		Oct 4	
Source	Syn.	Dodge	Syn.	Dodge	Syn.	Dodge	Syn.	Dodge
NMHC	2.40	3.00	2.06	2.80	2.40	2.94	2.19	2.59
CO	0.3	4.82	0.3	45.0	20.3	15.9	20.3	15.9
NO	0.234	0.235	0.270	0.273	0.235	0.230	0.214	0.215
NO_2	0.044	0.041	0.028	0.023	0.014	0.020	0.037	0.039
O_3	0.257	0.336	0.749	0.848	0.521	0.545	0.642	0.603

Note that the side-to-side NMHC ratios were: 0.80, 0.74, 0.82, and 0.85. The lower NMHC ratios and the absence of CO resulted in the first two runs being mismatched in reactivity. The higher ratios and the presence of CO at appropriate concentrations resulted in an excellent match in overall relative reactivity.

Aromatic Addition Experiment

The purpose of this experiment (July 15, 1982) was to provide a demonstration of the difference in reactivity of toluene and m-xylene in a background matrix of automobile exhaust. In each side, the added aromatic compound was 24% of the total carbon, while the other 76% of the carbon was from a direct injection from the Plymouth Volare using Phillips 66 regular gasoline. The data plot was shown on page 126. The sunlight was rather poor but the initial NMHC and NO_x were well balanced in this run. The side with m-xylene made five times the O_3 that was make on the toluene substituted side.

Relationship Between Gasoline and Exhaust Composition

The purpose of this section is to suggest to modelers further methods of dealing with the "un-speciated carbon" (*i.e.* the difference between the NMHC measurements and the sum of the GC measurements) in the chamber data. Because in most runs about 20% of the carbon was not classified as paraffin, olefin, or aromatic, significant flexibility is available to the modeler. This discussion seeks to place further constraints on that flexibility. The discussion begins with a further examination of the relationship between total class fractions in the gasolines and exhaust in dynamometer test data and in experimental data. Discussion then focuses on the relationships among individual species in the gasoline and exhaust, using MSERB data, UNC data, and literature information.

Total Class Fraction Relationships

The dynamometer test HC composition results were re-analyzed. Since it is clear that ethylene and propylene are produced in the combustion process, they were separated from the other olefins in this second analysis. The paraffin, non-simple olefins, and aromatic class fractions were then plotted for both the Plymouth Volare and Dodge Charger dynamometer tests conducted with the same gasoline and these are shown in Figure 30.

A general pattern is present in these results:

- the aromatic fraction in the exhaust tended to remain about constant or to slightly increase relative to the aromatic fraction in the gasoline;
- the paraffin fraction in the exhaust decreased relative to the paraffin fraction in the gasoline (except for the one cold high idle test of the Volare);
- the olefin fraction (other than the ethylene and propylene) in the exhaust tended to decrease or remain approximately constant relative to the olefin fraction in the gasoline;
- ethylene, propylene, and acetylene are formed in the exhaust.

Figure 31 shows HC class fractions produced from the Summary portion of the "spreadsheets" presented in the data section of Chapter 5. Except for the early 1982 data for the Plymouth Volare in which the aromatic fractions are quite large, the remaining run data are similar to that described above for the dynamometer tests. As was stated in the discussion on page 87, we now believe that the calibration factors for the PE900 gas chromatograph were giving high values in the analyses and thus increasing the relative fraction of NMHC accounted for by the aromatic species. This conclusion is further supported by the following discussion which suggests that the aromatic class fraction would be very nearly the same as that in the gasoline used.

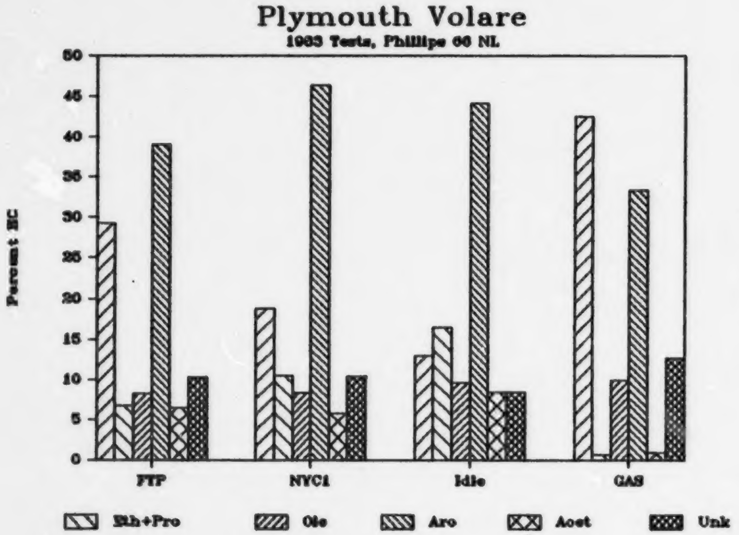
Individual Species Relationships

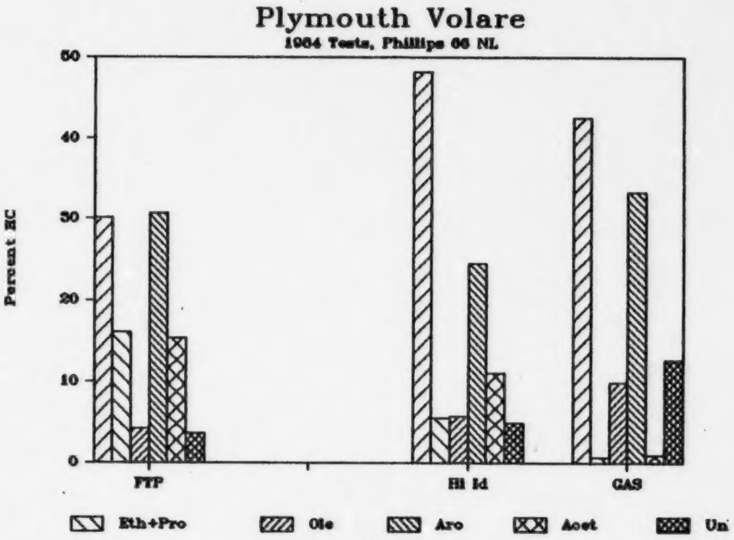
Figure 32 shows three plots, one for each HC class. Each plot compares the *average* carbon fraction of individual species (*i.e.* relative proportion of sum of total GC carbon) in exhaust from the 46-car VOC study[16] with the carbon fraction in a single analysis of the Union 76 gasoline used in the study. Both sets of analyses were performed by MSERB. The values plotted are listed in Table C9 in Appendix C. It should be noted that MSERB injected the gasolines into a bags containing background air. The data we received did not correct for any compounds present in the background of the bags, therefore, low, but significant, concentrations of species such as methane, ethylene and propylene were reported in the gasoline analyses. We made no corrections for these species.

In the plots in Figure 32, the paraffin compounds and the aromatic compounds showed a strong relationship of relative proportion in the gasoline to relative proportion in the exhaust. They showed little scatter, except for a few specific species. Other than ethylene, propylene, and 1-butene, the olefin compounds, however, showed a poorer defined pattern.

Likewise, Figure 33 compares the species carbon fractions of a single analysis of exhaust from the FTP test of the Plymouth Volare with the species carbon fractions from a single analysis of the Amoco Premium gasoline used in the test. (Again, MSERB performed both the exhaust and gasoline analysis). In these data, a pattern similar to that in Figure 32 was present, except there was more scatter in all plots, presumably because this was a single sample. Note that the Amoco Premium gasoline had nearly 20% toluene.

Similarly, Figure 34 compares the species carbon fractions of a single analysis of exhaust from the Dodge Charger with species carbon fractions of a single analysis of the Phillips 66 gasoline used in the test. Unlike the previous comparisons, the analysis of the exhaust HC species was performed by UNC and the analysis of the Phillips 66 gasoline was analyzed by MSERB. This difference in analysis methods





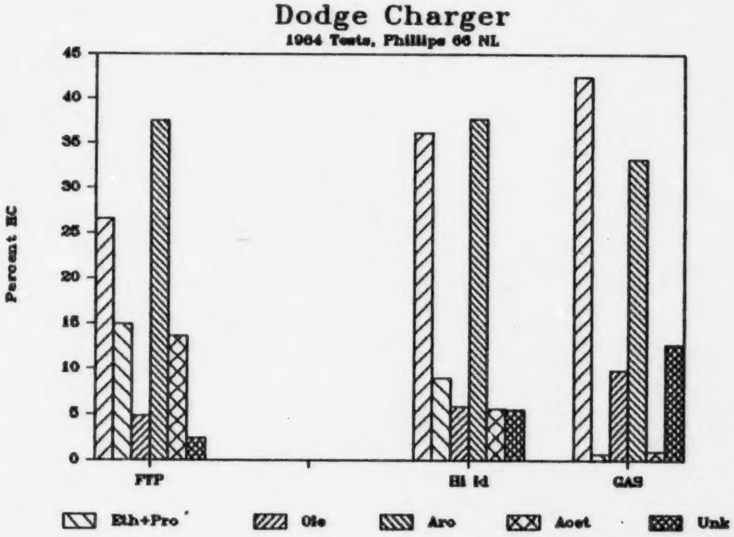
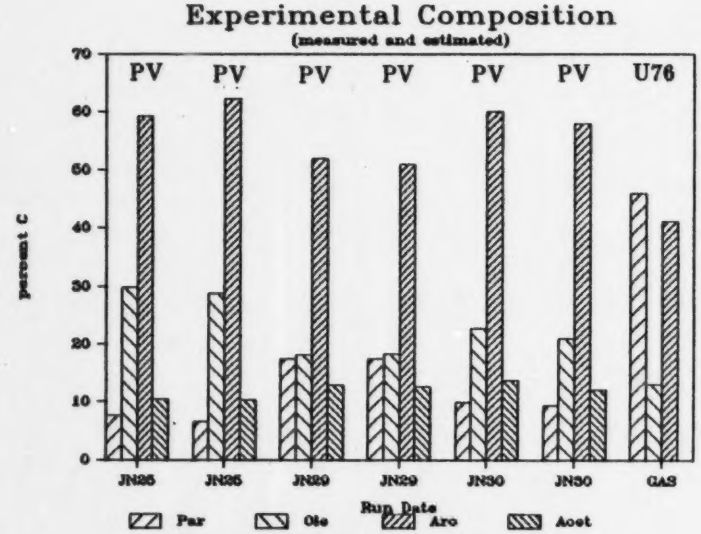
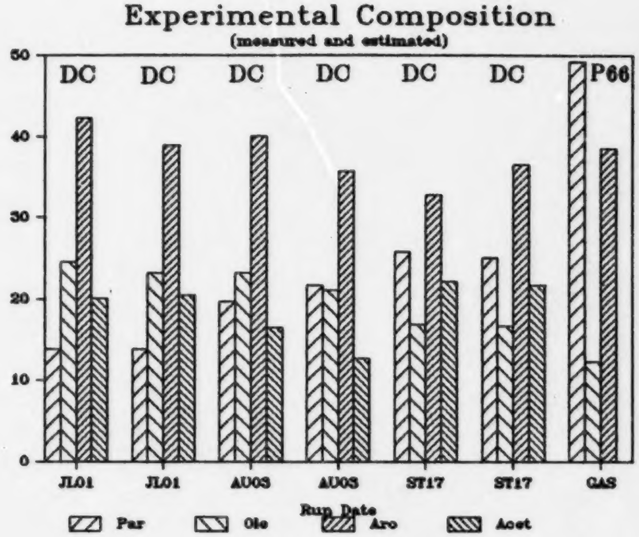


Figure 30. Exhaust hydrocarbon class composition (percent C) for MSB dynamometer tests of 1979 Plymouth Volare and 1972 Dodge Charger. Ethylene and propylene are separated from the higher olefins.





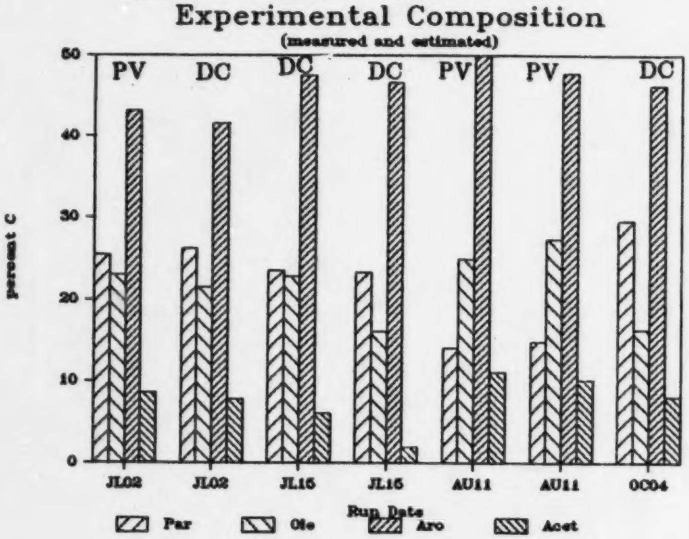
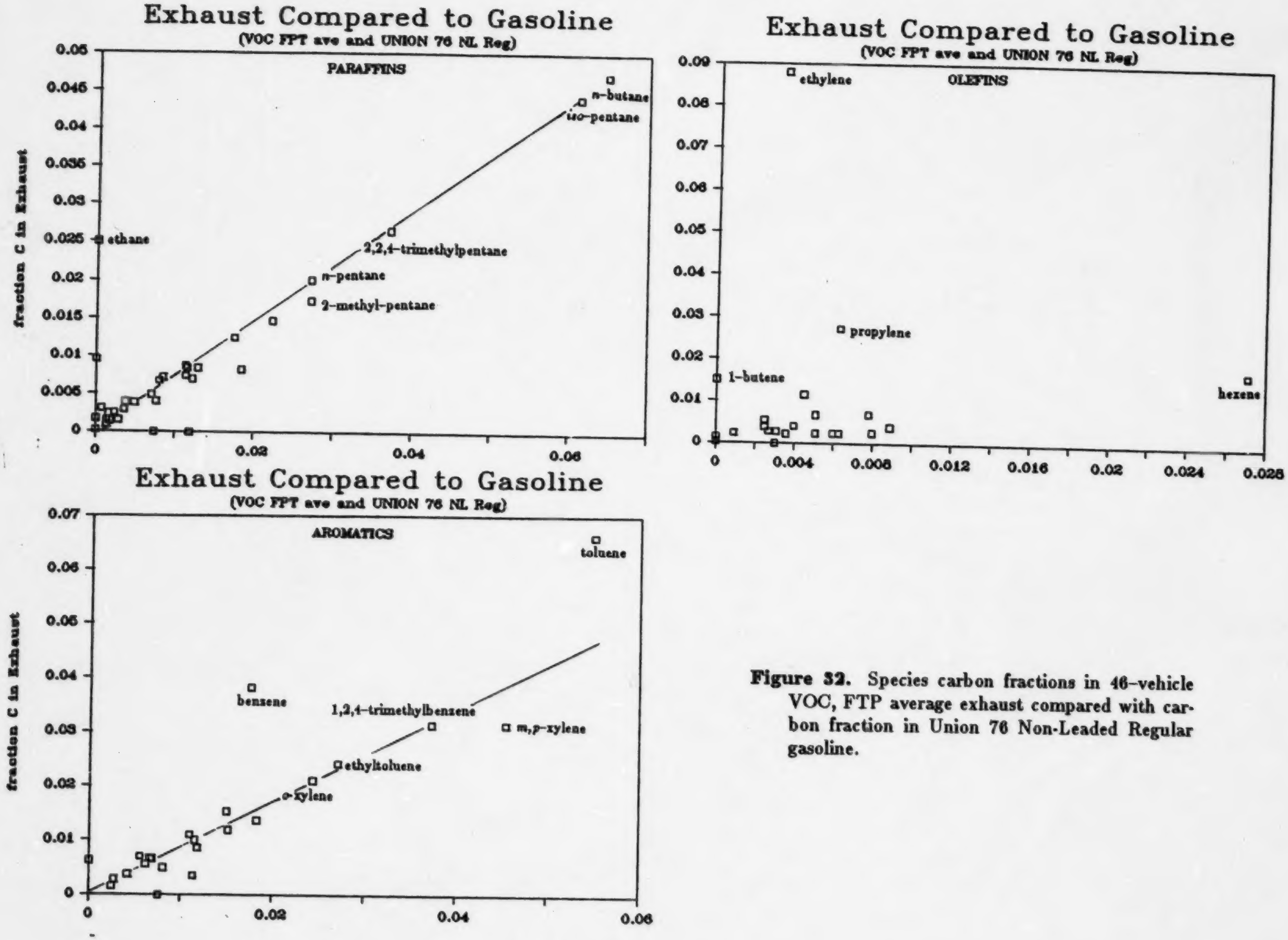


Figure 31 . Initial conditions hydrocarbon class composition for selected UNC chamber experiments. These include the measured species and the estimated classes of the unspeciated NMHC.



Exhaust Compared to Gasoline
(VOC FPT ave and UNION 76 NL Reg)

Exhaust Compared to Gasoline
(VOC FPT ave and UNION 76 NL Reg)

Exhaust Compared to Gasoline
(VOC FPT ave and UNION 76 NL Reg)

Figure 32. Species carbon fractions in 46-vehicle VOC, FTP average exhaust compared with carbon fraction in Union 76 Non-Leaded Regular gasoline.

resulted in more scatter in these data, nevertheless, there was still a definite strong pattern in the plots for paraffin and aromatic compounds.

From these figures, it is evident that:

- ethane and propane, which were not in the gasoline, appeared in the exhaust at 1–2% of the NMHC;
- the other paraffin compounds appeared at a ratio of approximately half their carbon fraction in the gasoline;
- ethylene, propylene, and 1-butene appear to be formed in the exhaust and the relative ratios among the three species were approximately constant for the three cases examined;
- the other olefins appeared at very low carbon fractions in the exhaust;
- in two samples benzene and toluene appeared at higher carbon fractions in the exhaust and in one sample (the premium gasoline with very high toluene), toluene appeared at a slightly lower relative carbon fraction in the exhaust than in the gasoline;
- the remaining aromatics appeared at slightly less than the relative fractions in the exhaust than in the gasoline.

A similar finding was reported by Nelson and Quigley.[24] In their study of 67 vehicles they found that the exhaust HC could be divided into three main types: combustion-derived olefins, fuel-derived components, and acetylene.

In their study, ethylene to acetylene ratios varied significantly, as they did in our data. Further, ethylene tended to be higher in vehicles that used engine modifications, such as spark retard. The Plymouth Volare generally produced more ethylene than the older Dodge Charger in our study.

In the Nelson study, the mass of the fuel-derived components in the exhaust, *e.g.* i-pentane, toluene, and m,p-xylenes, tended to have a positive, linear, low scatter relationship to the total mass of HC emitted. Acetylene tended to be much more scattered than the fuel- derived components, but also tended to exhibit a positive, linear relationship to the total mass of HC emitted.

Nelson was able to calculate the mass relationships among the fuel-derived com-

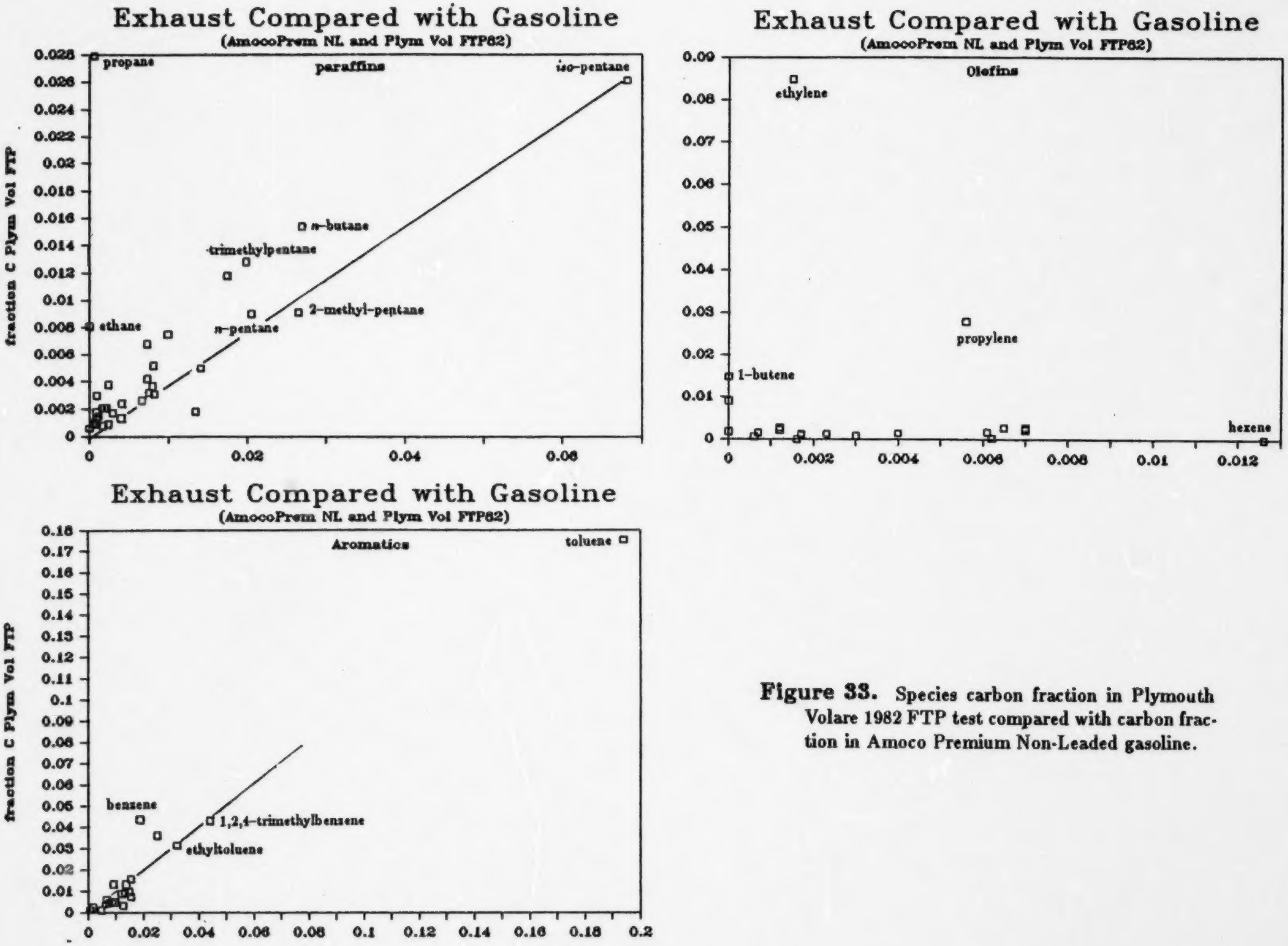


Figure 33. Species carbon fraction in Plymouth Volare 1982 FTP test compared with carbon fraction in Amoco Premium Non-Leaded gasoline.

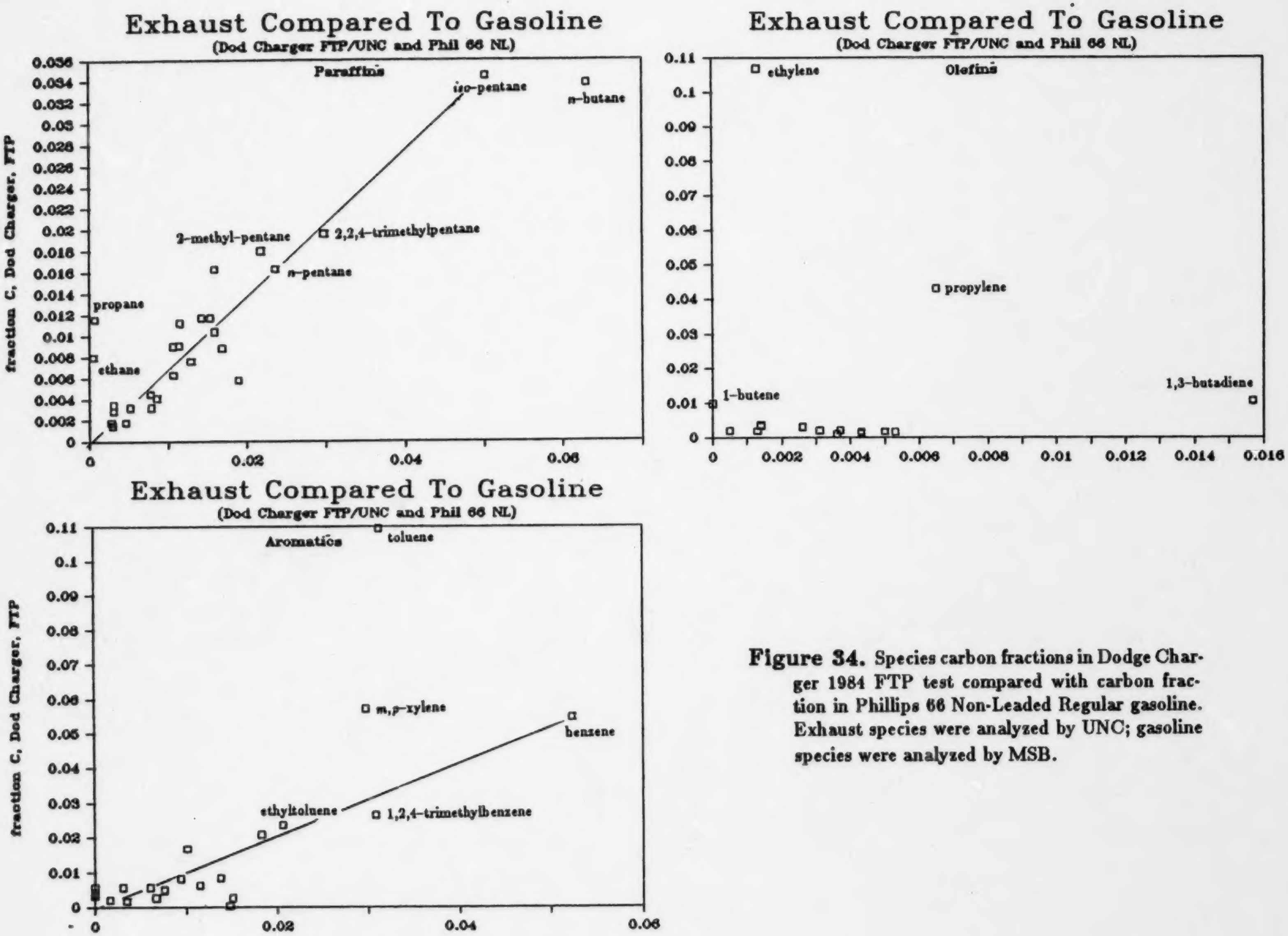


Figure 34. Species carbon fractions in Dodge Charger 1984 FTP test compared with carbon fraction in Phillips 66 Non-Leaded Regular gasoline. Exhaust species were analyzed by UNC; gasoline species were analyzed by MSB.

ponents. These were

$$\frac{\text{alkanes(ex)}}{\text{alkanes(fuel)} = 0.52 \pm 0.06}$$

and

$$\frac{\text{aromatics(ex)}}{\text{aromatics(fuel)} = 1.08 \pm 0.06}$$

and for

$$\frac{\text{(ex)}}{\text{(fuel)} = 0.59 \pm 0.16}$$

The exceptions to these relationships, *i.e.* n-butane, i-butane, and benzene were mostly likely formed by various radical recombination processes in the combustion process according to Nelson's discussion. He suggested that up to 30–40% of the butanes in the exhaust could be formed by the combustion process.

Nelson also calculated the same fractions for the data of Mayrsohn *et al.*[25] and found ratios of 0.62 ± 0.26 for alkanes and 1.06 ± 0.12 for aromatics.

Thus three different studies, the Mayrsohn study, the Nelson study, and the EPA VOC study all showed similar relationships among the HC species in the exhaust and the gasoline. It appears that, given the gasoline composition, the measurements of the combustion derived species (*i.e.* ethylene, propylene, n-butane, and benzene), measurements of a few fuel-derived species (*i.e.* tri-methyl-benzenes, i-pentane), and the relationships of Nelson's work, relative contributions of the remaining species could be calculated. Thus modelers, wishing to better partition the "un-speciated carbon," might attempt this type of analysis for the UNC chamber experiments.

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A

Facility Description

Chamber Description

Location

The site is approximately 32 kilometers from the University of North Carolina at Chapel Hill. It is in Chatham County, North Carolina and is approximately 10 kilometers from the small town of Pittsboro. Chatham County is one of the most rural, least industralized counties in North Carolina and is heavily wooded. The background concentrations of NO_x and nonmethane hydrocarbons are usually less than 5 ppb and less than 80 ppbC. More importantly, the air exhibits very low reactivity in the chamber.

Materials

The chamber surfaces are FEP Teflon. The film's transmission in the UV and visible regions of the solar spectrum is excellent, and it has only a few absorption bands in the IR, a property necessary to reduce the "greenhouse effect". It has a very low permeability for most chemical species and can be heat-sealed to form large durable panels. For this application its worst property is its ability to hold a static charge for long periods of time. Type A film, 0.13 mm thick is used.

Physical Design

Inlet and outlet doors, stirring fans, manifolds and other fittings come in through a solid floor. The sides are free for light entry. The floor of the chamber is elevated approximately 1.2 m to allow for easy access under the chamber.

The design is an A-frame 9.14 m wide, 12.10 m long and 6.10 m high at the peak on a plywood floor 1.22 m above the ground. Wooden beams, 5.08 cm by 20.32 cm, located on edge at 99.1 cm centers form an exterior framework on top of the plywood floor. Continuous 16.46 m lengths of film are attached to the inside by aluminum u-channels, screwed firmly to the wooden beams, thus compressing the film against the external support. See Figure 1 and Figure 2.

One piece, heat sealed Teflon film panels are used in such places as the triangular end panels and floors. The floor-to-side seals are achieved by a 0.61 m overlap of side panel film over floor panel film. A rubber strip under the film and an aluminum strip over top of the film complete the seal. All other seals are Teflon-to-Teflon under pressure of the aluminum u channel. A single unsupported heat sealed Teflon panel similar to the end panels is used to separate the chamber into two halves of equal volume. It is sealed to the floor and side panels in the same manner as described above. Aluminum foil is placed under the film on the floor to reflect the light and heat back up through the chamber. This is necessary to reduce solar heating of the air to a value that is within normal urban environments and to compensate for transmission losses through the Teflon film.

Orientation

The chamber is oriented with its long axis approximately north to south. The actual long axis orientation is along a 27–207 true heading. The orientation with respect to the sunrise and sunset at different times of the year and the altitude of the sun at noon for different times of the year are illustrated in Figure 3 and Figure 4.

Air Handling System

There are four air handling systems in each half of the chamber, one for exhausting, one for sampling, one for recirculating through dehumidifiers, and one for mixing. The exhaust system consists of two intake stacks, 0.61 m × 0.91 m intake doors, 0.61 m × 0.61 m exhaust doors, and an exhaust blower. The exhaust blower is a dual blower on a single shaft driven by a 1.5 horsepower motor. Air enters the system through the two 5.49 m high by 30.5 cm diameter stacks. This system is designed to permit rapid exhausting of chamber contents and replacement with

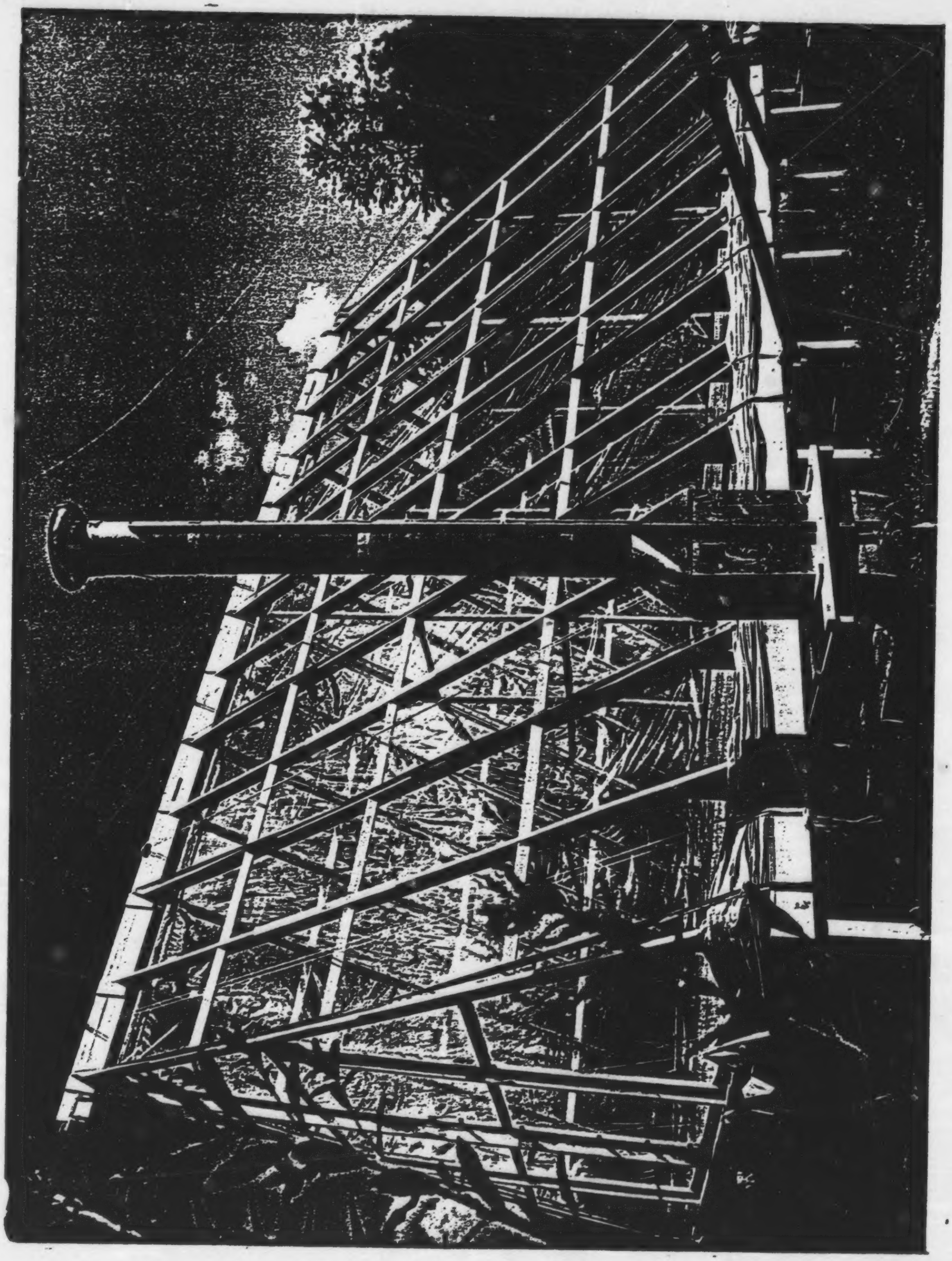


Figure 1. The University of North Carolina Smog Chamber. (Courtesy of the Greensboro Daily News)

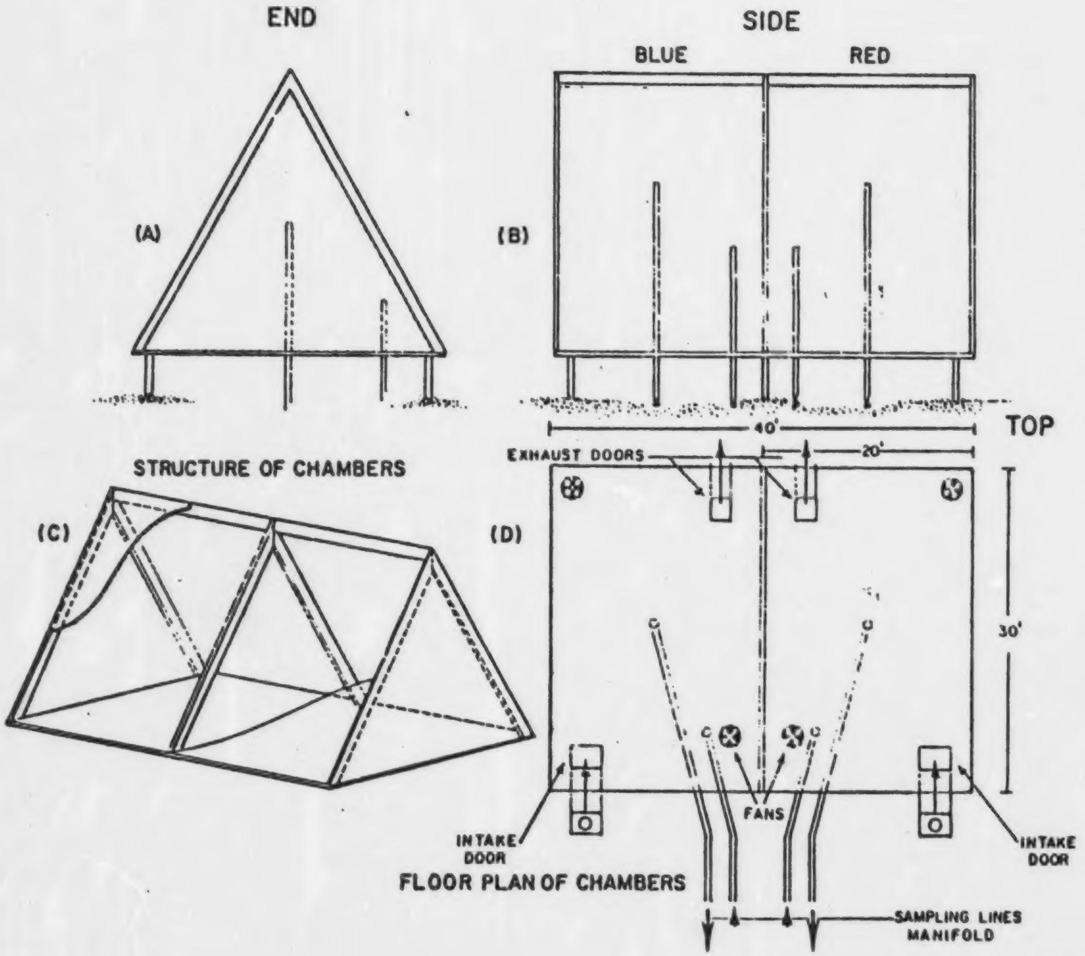
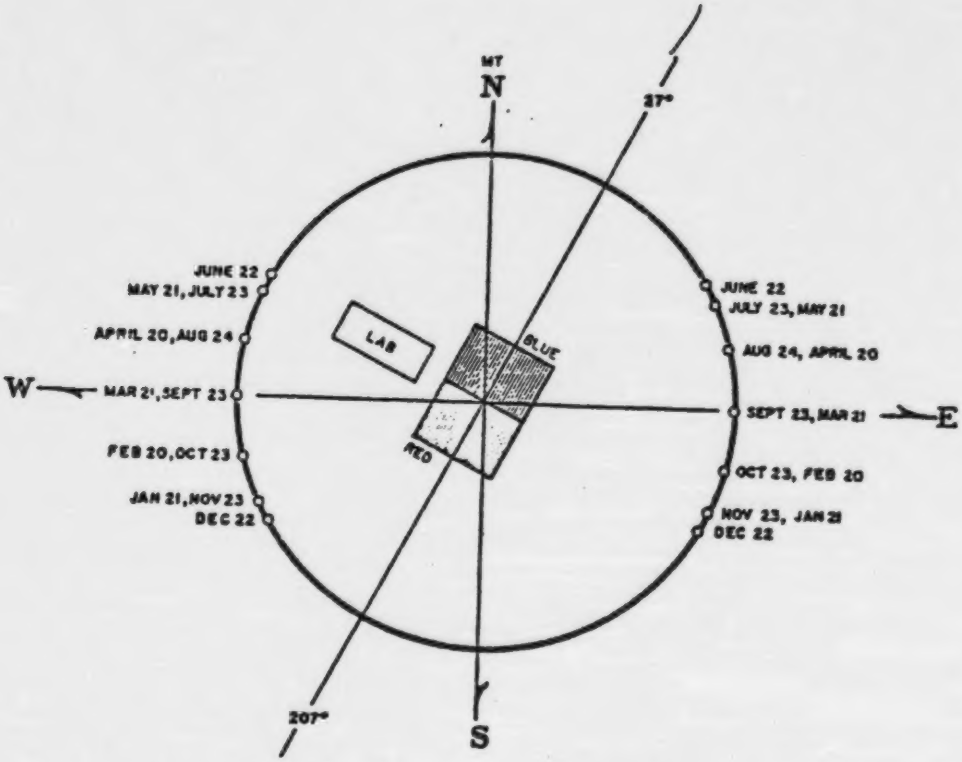

END
SIDE
BLUE
RED
(A)
(B)
40'
TOP
20'
EXHAUST DOORS
STRUCTURE OF CHAMBERS
(C)
(D)
30'
FANS
INTAKE DOOR
INTAKE DOOR
FLOOR PLAN OF CHAMBERS
SAMPLING LINES MANIFOLD

Figure 2. Schematic of UNC Outdoor Smog Chamber.


MT
N
27°
JUNE 22
MAY 21, JULY 23
APRIL 20, AUG 24
W
MAR 21, SEPT 23
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JAN 21, NOV 23
DEC 22
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BLUE
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JUNE 22
JULY 23, MAY 21
AUG 24, APRIL 20
SEPT 23, MAR 21
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NOV 23, JAN 21
DEC 22
207°
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Figure 3. Orientation of UNC Outdoor Smog Chamber with respect to seasonal sunrise and sunset positions.

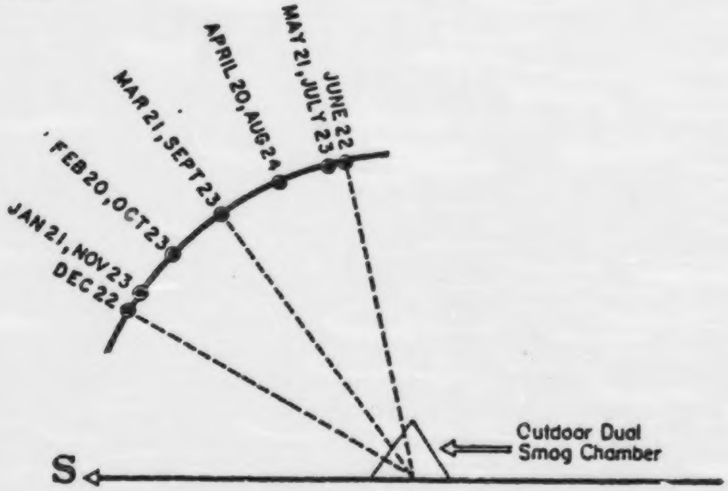

JUNE 22
MAY 21, JULY 23
APRIL 20, AUG 24
MAR 21, SEPT 23
FEB 20, OCT 23
JAN 21, NOV 23
DEC 22
Outdoor Dual Smog Chamber
S

Figure 4. Solar altitude and zenith angle at noon at the UNC Outdoor Smog Chamber for each month.

ambient air. The filling rate is 7190 l/min. The chamber can be flushed with a 99.6% decay of initial contents in 2 hours.

The second air handling or manifold system is for sampling and injection of pollutant materials into the chamber halves. To insure representative sampling, a 3.17 cm I.D. glass manifold runs from a point 1.83 m above the floor in the center of each chamber half down through the floor and over to a sampling laboratory. The sampling volume required by all the instruments does not exceed 5 lpm but to reduce losses due to long resident times it is necessary to have high flows in the manifold. The flow rate in the manifold is 60 lpm. The manifold system is wrapped with a controlled heating tape to maintain the sample slightly warmer than the chamber temperature. To avoid the necessity of makeup air, the sampling manifold is a closed loop. Squirrel cage blowers with housings and fans that are Teflon coated are used to circulate air through the manifolds. The unused sampler air is then returned through a 3.17 cm I.D. glass manifold to the chamber. These return manifolds provide a convenient method for injecting the initial reactants. There is also a special heated Teflon manifold for formaldehyde sampling.

Inside each chamber half are two mixing fans located in opposite corners. These provide circulation and mixing of the chamber contents. The fans are 50.8 cm diameter cast aluminum units that are FEP Teflon coated. They operate in a horizontal position, 0.76 m above the floor on 2.54 cm diameter Teflon coated steel shafts that extend through the chamber floor. Under the floor, 1/4 horsepower, 1750 rpm motors provide power through a belt and pulley system to each fan. Each fan operates at approximately 31.15 m^3/min.

Laboratory

The laboratory is adjacent to the chamber. It is a 3.66 m W by 15.24 m L by 3.05 m H temperature-controlled wooden structure oriented perpendicular to the chamber and 3.66 m away from it to avoid any shadowing.

The first 5.49 m nearest the chamber contain the instrumentation, manifolds, and calibration systems. At the sample inlet of each gas instrument is a three way Teflon AC solenoid valve. Since there are two intake manifolds (one for each chamber half), air from either manifold can be drawn through the three-way valve and into the instrument. In this manner timesharing of one instrument between the two chamber halves is possible.

The next 5.49 m contain the data acquisition computer system (described in the Data Acquisition System section) and the operations area. The last 4.27 m of the laboratory is a utility area with running water and storage facilities.

Gas tanks necessary to operate the instruments and perform calibration are located in a 1.22 m × 1.83 m room completely closed off from, but attached to, the laboratory. The injection system gas tanks and valves are housed in a second 1.52 m × 1.52 m well-insulated heated room adjacent to the end of the laboratory nearest the chamber.

Injection System

Pollutants are injected into the chamber sides via the return side of the sampling manifolds. The return manifolds enter the chamber sides under one of the mixing fans. The injection process uses gas cylinders containing pollutants at high concentration (1000–10,000 ppm range), two-stage stainless steel diaphragm regulators, on-off solenoid valves, and a precision needle valve. The flow rate of injected material into the manifolds is established by a mass flow meter with a 5 millisecond response time. The total injection volume is accurately controlled as a function of the time the solenoid valve is open. The open time of each solenoid valve is controlled by the computer system on command. Conditions can be varied sufficiently to have the injection time range from a few seconds for each component to 1–2 hours for a programmed injection used to simulate the buildup of pollutants in urban areas.

Data Analysis, Validation and Reporting

Data Acquisition System

A computer based data acquisition and control system (DAS) is used to acquire, process and record data for the chamber instrument system. The complete system is shown schematically in Figure 5.

Output signals from each instrument are wired to a crossbar scanner (or analog signal multiplexer). Under control of programs in the computer, the scanner connects the selected signal leads to the input of the digital voltmeter. The digital voltmeter, which has excellent noise and spurious signal suppression and can measure a 1 volt signal with a resolution of 10 microvolts, is triggered to acquire a reading and to supply the 5–1/2 digit binary coded decimal number to the computer. The

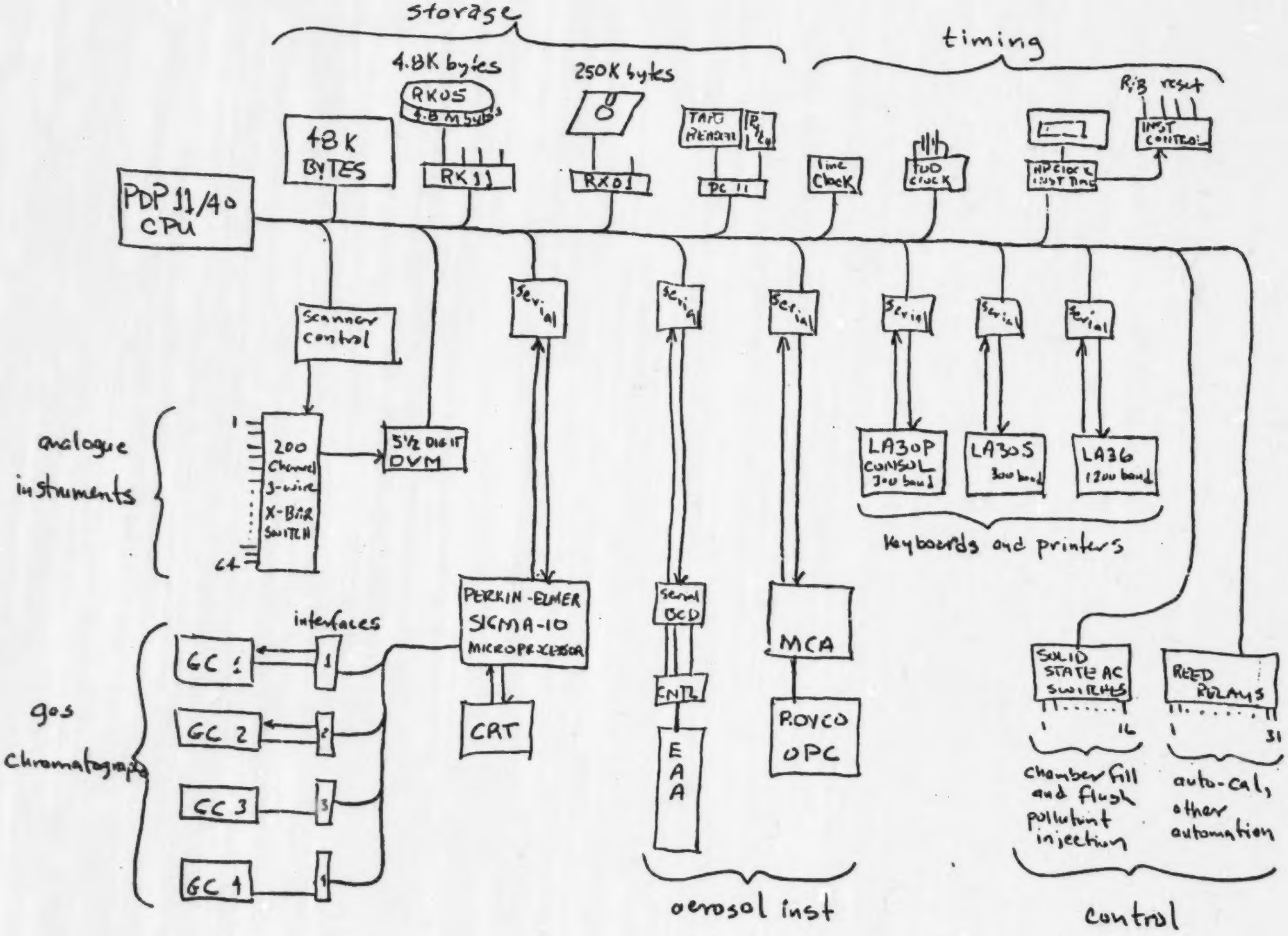

storage
timing
4.8K bytes
RK05
4.8 M bytes
250K bytes
48K BYTES
RK11
RX01
TAPE READER
PC11
line Clock
TOD clock
HP clock inst time
R;B reset
INST CONTROL
PDP 11/40 CPU
Serial
Serial
Serial
Serial
Serial
Serial
Scanner control
analogue instruments
1
200 Channel 3-wire X-BAR SWITCH
64
5½ DIGIT DVM
LA30P CONSOL 300 baud
LA30S 300 baud
LA36 1200 baud
keyboards and printers
interfaces
PERKIN-ELMER SIGMA-10 MICROPROCESSOR
gas chromatographs
GC 1
GC 2
GC 3
GC 4
1
2
3
4
CRT
Serial BCD
CNTL
E A A
MCA
ROYCO OPC
aerosol inst
SOLID STATE AC SWITCHES
1
16
REED RELAYS
1
31
chamber fill and flush pollutant injection
auto-cal, other automation
control

Figure 5 . Data Acquisition and Control System.

computer processes the information and then commands the scanner to move to the next channel and repeat the process. Further data processing is described below in the Data Treatment Procedures Section. The timing of the computer processes is under the control of a digital date and time-of-day clock which signals event times to the computer. Another digital timer operates the Teflon solenoid valve on the inlet of each instrument to connect the instruments to one chamber half during a given cycle of data acquisition.

This system provides fully automatic acquisitions and processing of data during a run and provides the operator with immediate, full data in physical units. Given this information about what is happening, the operator can then concentrate on what he wants to do. It also allows the massive amount of information generated during a run to be processed in a more effective manner after the run is over.

Standard Operating Procedure

Most experiments are initiated early in the morning by the site computer according to a detailed set of commands that have been programmed the night before. Prior to an experimental run the computer is programmed to automatically purge the chamber overnight with background ambient air. Several hours before dawn the DAS begins recording measurements of the background concentration. Single instruments are timeshared on an alternating four minute cycle between the two sides. The chamber intake and exhaust doors are then sealed by the computer and the drying fans in each side of the chamber activated to reduce humidity and minimize chamber wall effects. Finally, the initial concentrations of reactants of interest are injected before sunrise. To do this, the computer selects the proper tank and calculates the correct time to achieve the desired initial concentrations. Injections are normally short "slug" injections; most experiments have initial hydrocarbon, NO, and NO_2. Monitoring of the chemical and physical species mentioned earlier continues usually until 1900 EDT when the experiment is terminated. The computer then performs several close-down procedures, including turning off certain instruments, opening chamber vent doors, and turning on the exhaust fan to purge the chamber. If instructions for the next experiment have not been programmed during the day, the operator does so at this time.

Variations of the standard operating procedures include: 1) not changing humidity before the experiment, 2) injecting pollutants slowly during the experiment, 3) diluting the chamber(s) during the experiment to simulate mixing height profiles,

4) transferring the contents of one chamber side to the other, and 5) injecting initial conditions into the chamber containing part or all of the product of a day-old experiment. Most pollutants are injected from high concentration gas cylinders (10,000 ppm) which can be controlled by the computer. Some pollutants are liquids with vapor pressure too low to have a high vapor concentration cylinder prepared, and are injected manually. Carefully measured samples are heated in a U-tube in which warm zero air is passed through to the return manifold.

Data Treatment Procedures

General

The operations are carried out on four different computers and the Broomall plotter. The PDP 11/40 is at the chamber site and is responsible for acquiring the data. The LSI/11, the VAX, the IBM 370/360, and the Broomall plotter are on campus grounds, and complete the data treatment procedure after a run.

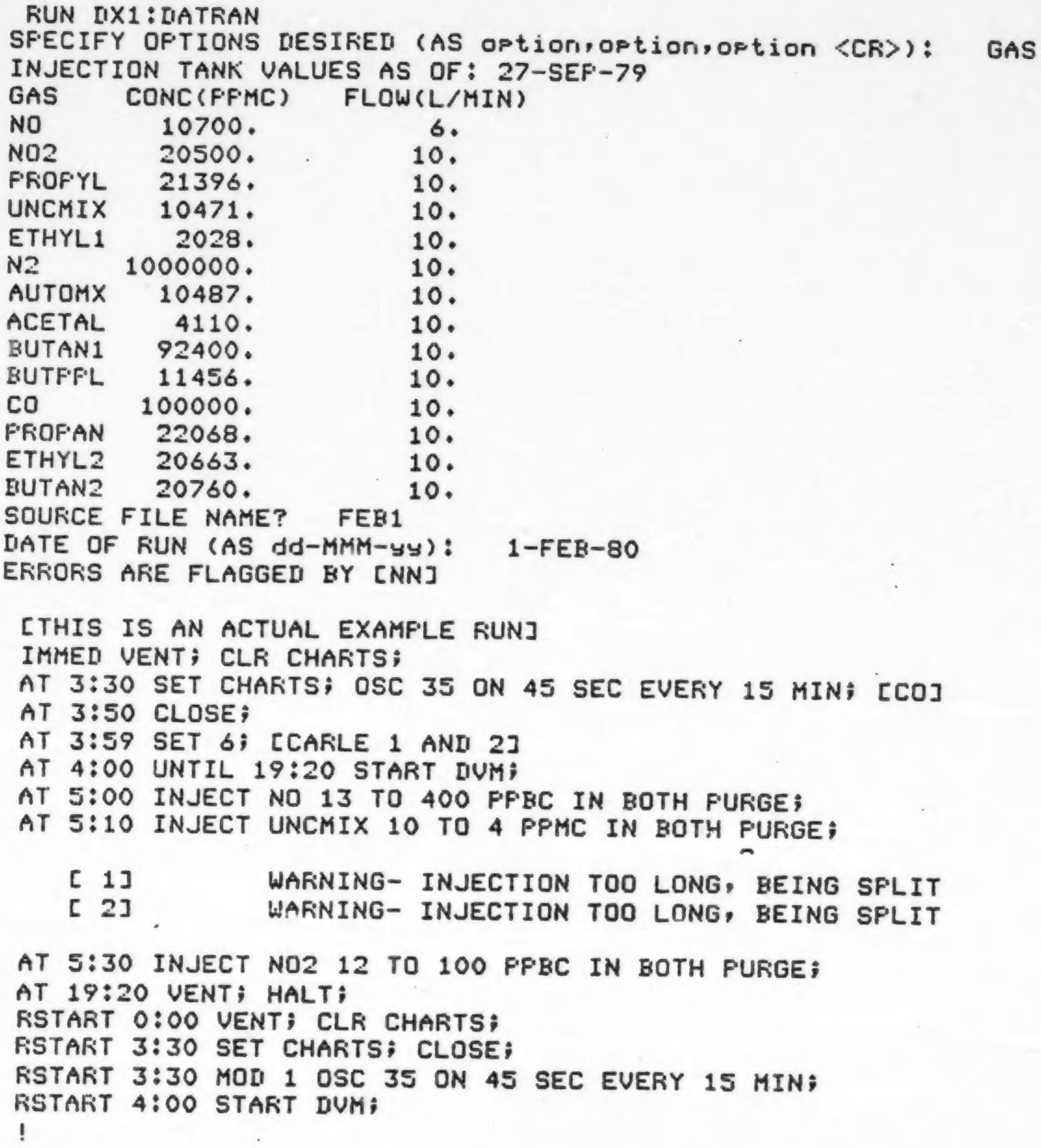
During A Run

DATCOL and DATRAN are written in assembly language and PASCAL. DATCOL performs several functions, such as accepting instructions from the keyboard and interpreting a command file which prepares the chamber, makes injections, turns on the necessary instruments, and finally purges the chamber and turns off the instrumentation at the end of the experiment. Command files can be written in an easily readable English text style. An example is shown in Figure 6. DATRAN translates this file into a format which DATCOL can interpret. DATCOL also controls the data acquisition process, and records:

1) the instrument analog outputs;
2) the GC files produced by the Perkin Elmer Sigma 10 GC integrator and processor;
3) the adjustment file (computer readable instructions for data adjustment); and
4) the comments files,

all on the RK05 hard disk. It also maintains status information to restart and continue an experiment after a power failure.

The operator has several choices for printing data with DATCOL. He can have the data printed during the whole experiment, print data for only selected times



```
 RUN DX1:DATRAN
SPECIFY OPTIONS DESIRED (AS option,option,option <CR>):   GAS
INJECTION TANK VALUES AS OF: 27-SEP-79
GAS     CONC(PPMC)   FLOW(L/MIN)
NO        10700.          6.
NO2       20500.         10.
PROPYL    21396.         10.
UNCMIX    10471.         10.
ETHYL1     2028.         10.
N2      1000000.         10.
AUTOMX    10487.         10.
ACETAL     4110.         10.
BUTAN1    92400.         10.
BUTPPL    11456.         10.
CO       100000.         10.
PROPAN    22068.         10.
ETHYL2    20663.         10.
BUTAN2    20760.         10.
SOURCE FILE NAME?   FEB1
DATE OF RUN (AS dd-MMM-yy):   1-FEB-80
ERRORS ARE FLAGGED BY [NN]

 [THIS IS AN ACTUAL EXAMPLE RUN]
 IMMED VENT; CLR CHARTS;
 AT 3:30 SET CHARTS; OSC 35 ON 45 SEC EVERY 15 MIN; [CO]
 AT 3:50 CLOSE;
 AT 3:59 SET 6; [CARLE 1 AND 2]
 AT 4:00 UNTIL 19:20 START DVM;
 AT 5:00 INJECT NO 13 TO 400 PPBC IN BOTH PURGE;
 AT 5:10 INJECT UNCMIX 10 TO 4 PPMC IN BOTH PURGE;

    [ 1]         WARNING- INJECTION TOO LONG, BEING SPLIT
    [ 2]         WARNING- INJECTION TOO LONG, BEING SPLIT

 AT 5:30 INJECT NO2 12 TO 100 PPBC IN BOTH PURGE;
 AT 19:20 VENT; HALT;
 RSTART 0:00 VENT; CLR CHARTS;
 RSTART 3:30 SET CHARTS; CLOSE;
 RSTART 3:30 MOD 1 OSC 35 ON 45 SEC EVERY 15 MIN;
 RSTART 4:00 START DVM;
 !
```

Figure 6 . Sample DATCOL Command File.

during the experiment, have earlier data printed, or not print data at all.

The operator can also, at any time during the experiment, enter through the keyboard information such as calibration corrections for any instrument or that an instrument is not functional and for what time interval this information applies. This type of information is entered by DATCOL into an Adjustment file. This file can be read and interpreted by other computers and can be directly applied to correcting and processing data in later steps. The operator can at any time also enter general comments through the keyboard which DATCOL stores in a Comment file. Such information, when transferred along with the digital data, greatly aids in processing.

Strip charts are operated for almost every instrument as a back-up to the computer.

Data Processing Steps

Data processing involves three types of staff

- **Project Coordinator (PC)**—senior staff, makes judgements about data quality, decides on calibration factors, gives directions to other data processing staff; uses computer run tracking system to direct attention of PPs and to CTs to work that is needed by indicating the status of processing in the run tracking data base;
- **Peak Peaker (PP)**—seasoned staff, skilled at converting strip chart peaks into computer files using a high-resolution electronic digitizer pad connected to a computer; throughly familiar with the data output of each chromatograph; makes plots of digitized data for QA by PC; corrects picking mistakes by examining the raw data plots; basically works independently using computer reports from run tracking system to indicate needed work; updates run tracking system to move work to next stage;
- **Computer Technician (CT)**—staff, highly skilled at use of various computer systems (LSI-11/23, IBM PC, VAX-11/780, IBM 4341), with a through knowledge of file transfer and storage among these systems; responsible for running programs that read and convert site floppies into input for other processing programs; responsible for creating, naming, and backing up to magnetic tape all data files on all systems; in addition, the CT is usually an apprentice processing program developer and maintainer.

Data processing is organized by the type of data. The major processing effort occurs for the chromatographic type instruments. Data processing for the continuous instruments (DVM data) is less difficult than the chromatographic instruments, because the data come from the site in digital form. Both of these processing streams, however, depend upon having calibration factors to convert the voltages and raw displacements into physical units of concentration.

The "auto-cals" can be automatically stripped from the DVM data by the CT who moves the data from the site floppies. These stripped cals can be processed rather quickly by computer programs once the calibration source concentrations are known. The chromatographic calibration data, however, must be examined by a PC, picked by a PP, and stored by a CT to await the development of calibration source concentrations. Furthermore, each instrument may have 10 specie calibration factors.

Table 1 illustrates, in a flowchart, the stages in processing the GC instrument data. The flow of processing in these charts is from left to right. The three letter codes describe events in processing the data and the lines indicate which events depend on other events having occurred. As the processing events occur, the three-letter codes are entered into the on-line run processing tracking system by whoever did the step. Simple commands allow the PC, PP, and CT to create appropriate printed reports showing which runs and which instruments are at which stages of processing.

Table 2 similarly shows the flowchart for processing DVM data. Some of the processing steps for the DVM "auto-cal" data occurs on this chart also. The same program that makes the "Raw Plot" also strips the "auto-cals" into a separate file (the ACS–Auto Cals Stripped—event on the chart). These data are then processed by a program that results in a data file of instrument span responses and instrument zero values for the O_3 and NO_x monitors. An example list of these will be shown in the next section.

Once the actual run concentrations are known for both the HC and the NO_x, the run documentation, to be included in the combined data file, can be written. Here all aspects of the run are drawn together to provide a description of the run, its quality, problems, and outcome.

Table 3 illustrates the events in the documentation and in the creation of a single *segmented* file containing all the data for the run in a uniform format.

Table 1

Processing System for Instrument Data

```
    !NTB!
   /
tot inst  __ cal processing_
  \      /                   \
    !PID!                    !CFD!        <HRU>__
        \                         \     /        \
         \                         <CRU> -------- !CQA!---- (F2V)---- (V2U)
          \                       /
          <PRU>---- <FPT> --!PQA!
```

!sss! == stages determined by Project coordinator (PC)
<sss> == stages determined by Peak Pickers (PP)
(sss) == stages determined by Computer Techs (CT)

Pers	RUNENTRY stages	Meaning
PC	PID : Pick inst det	Charts marked, Inst status sheet in folder
PC	NTB : Not to be proc	No futher processing marked on Inst Status sheet
PC	CFD : Cal fac det	Cal factors for each comp entered on Inst status sheet in folder
PP	PRU : Pick run	Data has been digitized and P-file exists
PP	FPT : FPlot done	P-file has been plotted and plot is in folder
PC	PQA : FPlot QA	Fast plot has been marked OK (no bad data points in P-file)
PP	CRU : CALCON run	C and K files exist on floppies
PP	HRU : HCANAL run	HC analysis printout in run folder
PC	CQA : Comp CS QA	Instrument QA completed on C and K files Initial Conditions updated
CT	F2V : File 2 VAX	C and K files moved to VAX
CT	V2U : Ready 2 merge	C files merged together, K files merged together
PC	BAD : Stop processing	Something is wrong with this data

Table 2

Processing System for DVM Data

```
 cal processing
 /             \
tst runs       (CFS)-------
 \             /             \
  \      (ACS)                \
   \     /                     \
   (URU)------(RPC)----!PQA!-<DRU>--!CQA!--!R2M!
        \                      /
        (UTV)                 /
              \              /
              (V2T)-------
```

```
!sss! == stages determined by Project coordinator (PC)
<sss> == stages determined by Peak Pickers (PP)
(sss) == stages determined by Computer Techs (CT)
```

DVM data processing steps

Pers	Step	Meaning
CT	URU : Unpack run	Site floppy data expanded to ASCII Ufiles
CT	U2V : Data to VAX	Ufiles moved from LSI disk to VAX
CT	V2T : to archive tape	Data moved from VAX to tape
CT	RPC : Raw Plot done	Plot of voltages to examine data
PC	PQA : Plot QA	Initial quality check
CT	ACS : AutoCals strip	Cals separated for processing
PC	CFS : Cals done	Calibration factors determined
CT	DRU : DVMFIX run	Voltages changed to concentrations
PC	CQA : Conc QA	Concentration Quality Assurance
CT	R2M : Ready 2 merge	Merge process on VAX can be run
PC	NTB : Not to be proc	Not to be processed
PC	BAD : Stop processing	Something is wrong with this data
CT	NDV : No DVM data	

Table 3

Documentation and Final File Production Steps

DOCUMENTATION data processing steps

Pers	Step	Meaning
PC	SUM : Run sum done	DVM, Instrument, and Raw Quality Combined.
CT	D2V : Doc to VAX	Documentation transferred to VAX
PC	DQA : Doc QA	Documentation Quality Assurance

FINAL FILE data processing steps

Pers	Step	Meaning
CT	MR3 : Merged 3 sect	Merge pieces to final file
CT	ALT : Files to tape	Ascii labeled tape made
CT	FPC : Final plot done	Correct conc plot made
PC	FQA : Final QA	Final Quality Assurance
PC	NTB : Not to be proc	
PC	BAD : Stop processing	Something is wrong with this data

GC Calibration Processing

The GC instrument calibration processing is complex enough to require its own tracking system. Table 4 gives the flowchart for these calibration data.

A major time-consuming task on this chart is the Official Calibration Source (ocs) event. This event signals the existence of an ocs form that names a source and describes the concentration of each specie in the source. These paper forms are the results of the manual calibration comparisons described above. Filling out the form requires extensive analysis and reconciliation to arrive at a *certifiable* set of concentrations in the calibration sources. The OCS form requires the validation date and name of the individual certifying the calibration source.

These OCS values are entered into another data base and appropriate S-files (source concentration) files are created. These are used as input to the CALFAC program to match the instrument responses (stored in R-files by the PP) with the calibration sources to compute the calibration factors for each species. These calibration factors are, in turn, entered into another data base and its output is a file of calibration factors that are subjected to graphical and statistical analysis by the CALANA (calibration analysis) program. Using these plots and statistics, and other information such as the manual injections, and previous calibrations calculated for runs nearby, the PC selects a calibration factor for each instrument-species.

The actual calibration factors used in processing the runs are entered into another data base and reports of these are available for plotting and further analysis. The actual factors are also included in the automatic program documentation produced by the DVMFIX and CALCON programs (K-files) and are included as a permanent part of the documentation section of the segmented file.

Table 4

Processing System for Instrument Auto-Calibration Data

```
tot inst    cal analysis
      \    /            \
       !CPI!            !OCS!
           \                \
            \                \
             <DPR>----------<CFR>--(Q2V)--(DTR)--(C2L)--<CLR>--!CQA!
```

!sss! == stages determined by Project coordinator (PC)
<sss> == stages determined by Peak Pickers (PP)
(sss) == stages determined by Computer Techs (CT)

Step	CALENTRY stages	Meaning
PC	CPI : CAL pick Inst	Charts marked, cal status sheet in folder
PP	DPR : Digpik run	Cal data digitized and R-file exists
PC	OCS : OCS ok	Official Cal Source exists in DTR
PP	CFR : CALFAC run	Cal Factor computed, Q-file created
CT	Q2V : Qfile to vax	Q-file moved to VAX
CT	DTR : DTR file updated	Cal Data added to DTR data base
CT	C2L : Cals to LSI	DTR CAL file loaded on LSI-11
PP	CLR : CALANA run	Cal Factors analyzed
PC	CQA : Cal QA	Cal Factor Quality Assurance
PC	NTB : Not to be proc	Not to be processed
PC	BAD : Stop processing	Something is wrong with this run

B

Analytical Methods

Introduction

The analytical instrumentation in the gas laboratory adjacent to the large outdoor chamber at UNC includes: six packed column and two capillary gas chromatographs for hydrocarbon, organic nitrate, and inert tracer analysis; one liquid chromatograph for DNPH-aldehyde analysis; an automated wet chemical formaldehyde instrument; two ozone and NO_x chemiluminescent monitors; and one UV ozone photometer. The laboratory also contains all of the associated calibration systems used for these instruments. In addition, solar and UV radiation sensors are mounted on top of a 7 meter tower next to the laboratory. Chamber temperature measurements are made with an inline thermistor located in the inlet of each chamber sampling manifold. The manufacture and calibration methods for all of these systems are listed in Table 1 and Table 2. A list of the species measured on each site instrument is given in Table 3.

Hydrocarbons

Total hydrocarbons (THC), methane (CH_4) and carbon monoxide (CO) are analyzed with a Beckman 6800 gas chromatograph. Figure 1 shows a typical Beckman 6800 measurement cycle. This cycle occurs every 5 minutes and each side of the chamber is sampled for 30 minutes. Unfortunately, methane responds differently than non-methane HC on this type instrument requiring a separate methane calibration as well as a NMHC calibration.

Table 1 . Analytical Methods, Characteristics, and Operation Methods

Substance	Method	Manufact and Model	MDC	Range	Mode	Time Shared
O3	Chemiluminescence	Bendix 8002	0.001	0-2	Continuous	Yes
NO, NO$_x$, NO$_2$	Chemiluminescence	Bendix 8101-B	0.005	0-1	Cyclic, 4 min	Yes
HC's alkenes,alkanes, aromatics	Automated multiple column GC-FID	Carle 211	0.005-0.010	0-100	Cyclic, 15 min	Yes
THC, CO, CH4	Automated multiple column GC-FID	Beckman 6800	0.010	0-30	Cyclic, 15 min	Yes
HCHO	Automated Colorimetic(reverse West-Gaeke)	CEA 555	0.01	0-2	Continuous	Yes
Acetaldehyde, propionaldehyde, MEK	Automated multiple column GC-FID	Carle 211M	0.02-0.05	0-100	Cyclic, 30 min	Yes
Aromatics HC, aromatic aldehydes, phenols	GC-FID	Perkin-Elmer 900	0.010	0-100	Manual	Yes
Halocarbon tracers	GC-EC variable freq. pulsed bais detector	Analog Tech. Corp.	0.0004	0-1	Cyclic, 30 min	Yes
PAN and Alkyl nitrate	GC-EC DC based EC Model 940	Varian Aerograph	0.0003-0.0008	0-1	Cyclic, 30 min	Yes
HNO3	Chemiluminescence, molybdenum converter, nylon scrubber	Bendix 8101-B	0.003	0-1	Cyclic, 15 min	No
H2O2	sample taken manually with bubbler; analysis using automated chemilum. method		0.0001	0-1	Manual	Yes
Temperature	Thermistor	YSI	0.2°F	20-110°F	Continuous	No
TSR	Pyranometer	Eppley Black and White	0.001 Langly	0-2 Langly	Continuous	No
UV	Pyranometer	Eppley UV	0.1 mLangly	0-100 mLangly	Continuous	No
Dew Point	Cooled mirror	EGandG 880	0.1°F	-40 to 120°F	Continuous	Yes

Table 2 . Calibration Sources for Gases

Species	Source	Calibration Method	References
O_3	UV-quartz O_3generator	UV photometry Dasibi Model 1008-AH	EPA
NO	Cylinder O_3UV photometry	Certified commercial analysis and transfer via Gas Phase titration	EPA
NO_2	Oxidaton of NO	Gas Phase Titration	EPA
CH_4, CO, THC	Cylinder	Certified commercial analysis	EPA
HC's	Cylinder	Certified commercial analysis	EPA
HCHO	paraformaldehyde and 37% HCHO	Prepared static calibration standards verified with chromotropic acid bubbler technique	
Acetaldehyde, propionaldehyde, MEK	pure compounds	Prepared static calibration standards	
Aromatics	pure compounds	Prepared static calibration standards	
PAN	PAN purified	Reference method and transfer standard	Winer, A. *et al.* EST 8 p1116, (1974)
Alkyl nitrates	pure alkyl nitrates	Prepared static calibration standards	
HNO_3	HNO_3 (gaseous)	Dynamic source (gas) calibrated by colorimetric (chromotropic acid) bubbler method	Spicer, C., Adv. Envr. Sci. and Tech. 7 p163 (1980)
H2O2	liquid H2O2	Liquid standards and iodometric analysis	

Table 3.

Species Measured by Major Site Instruments

- Bendix Ozone Monitor
    - Ozone
- Bendix Nitrogen Oxide Monitor
    - nitric oxide, NO
    - nitrogen dioxide, NO_2 and PAN
    - sum, NO_X
- CEA Formaldehyde Monitor
    - formaldehyde
- Carle I FID Gas Chromatograph
    - C_3 to C_8 alkanes
      e.g. propane, butane, isopentane, pentane, 2-methylpentane, 2,2,4-trimethylpentane, octane
    - C_6 to C_8 aromatics
      e.g. benzene, toluene, m-xylene
    - C_2 to C_8 alkenes
      e.g. ethylene, propylene, 1-butene, cis-2-butene, trans-2-butene
    - acetylene
    - Total Hydrocarbon
- Carle II FID Gas Chromatograph
    - methane
    - ethane
    - propane
    - ethylene
    - propylene
    - acetylene
    - acetaldehyde
    - propionaldehyde
    - acetone
    - methylethylketone

Table 3.

- Carle III FID Gas Chromatograph
  - ▷ C_3 to C_5 alkanes
    e.g. propane, butane, isopentane, pentane
  - ▷ C_3 to C_5 alkenes
    e.g. ethylene, propylene, isobutene, 1-butene, cis-2-butene, trans-2-butene
  - ▷ C_8 to C_{10} alkanes
    e.g. octane, 2,2,4-trimethylpentane
  - ▷ C_6 to C_9 aromatics
    e.g. benzene, toluene, m-xylene, o-xylene, 1,2,4-trimethylbenzene
  - ▷ methanol
- Varian ECD Gas Chromatograph
  - ▷ PAN
  - ▷ alkylnitrates
  - ▷ biacetyl
  - ▷ tracers
    e.g. CCl_4, C_2Cl_4, $C_2Cl_3F_3$
- Perkin Elmer 900 FID Gas Chromatograph
  - ▷ C_6 to C_{12} aromatics
  - ▷ aromatic oxygenates and nitrogen-containing products
- Perkin Elmer Sigma 2 FID Gas Chromatograph
  - ▷ C_3 to C_{12} alkanes
    e.g. propane to dodecane
  - ▷ C_3 to C_6 alkenes
    e.g. propylene to hexene
  - ▷ C_6 to C_{12} aromatics
    e.g. benzene to dimethylnapthalene
  - ▷ aromatic oxygenates and nitrogen-containing products
- Beckman 6800 NMHC, Methane and CO FID Gas Chromatograph
  - ▷ Total Hydrocarbon
  - ▷ methane
  - ▷ CO

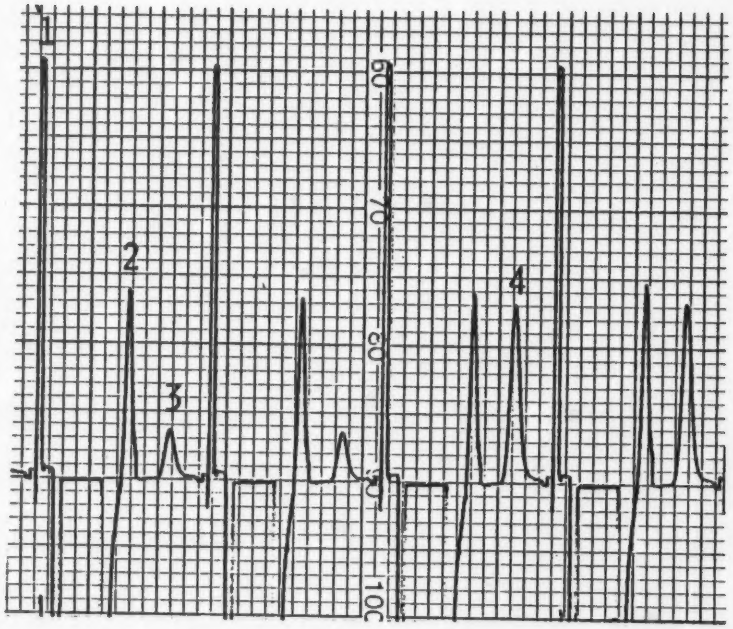


Figure 1. Example Chromatograms from Beckman 6800 Gas Chromatograph. Peaks: (1) Total Hydrocarbons — 4.0 ppmC, Attenuation × 2; (2) Methane — 2.5 ppmC, Attenuation × 1; (3) CO — 9.9 ppmC, Attenuation × 2; (4) CO — 37.2 ppmC, Attenuation × 2.

A manually operated six port Carle mini-valve (Carle Instruments, Inc., Anaheim, Calif. Model Mk. II, Cat. No. 5621) on a Carle 211 gas chromatograph (designated Carle I) is also used to obtain total hydrocarbon data. This system introduces a sample directly into a blank column and then to the FID. Figure 2 shows how this instrument is used to match the THC injected in the two chamber halves. The increase in the chamber THC is clearly shown as well as the degree of relative matching of the two chamber sides. This THC method is used primarily in the morning during injection and the regular operation of the Carle I is used for the rest of the run. By characterizing the response to zero air and methane through this system, and measuring methane separately on another column, it is possible to subtract the air and methane response from the THC response and obtain NMHC concentrations. The exact procedure that we have used is described in detail in Appendix D.

Three automated Carle Model 211 packed column FID gas chromatographs are used for C_1–C_{10} analysis. The first of these chromatographs, Carle I, is used to perform a gross analysis on C_2–C_{10} hydrocarbons. Three chromatographic columns perform the analytical separation. An additional 2' × 1/8" column of carbowax 400 was installed just before the flame detector to balance column bleed and prevent excess baseline displacement after valve switches.

The columns used in Carle I are:

Column 1	6' × 1/8" carbowax 1540 + 5% Apeizon L on Supelcoport 80/100 mesh support to separate C_6–C_8 paraffins, olefins and aromatics
Column 2	6' × 1/8" N-octane/Poracil C 100/120 mesh (baked at 240°C for 2 hrs.) + 2' × 1/8" 20% Apeizon L on Supelcoport 80/100 mesh to separate C_4 and C_5 olefins and some C_6 paraffins
Column 3	2' × 1/8" FL alumina treated with 5% NaCl to separate C_1–C_3 compounds.

Bidirectional electric motors (Carle model 4201) are used to actuate 6-port mini-valves and these shunt the sample to the appropriate columns. The valves are controlled by a 30 minute 110 volt Carle programmable timer (Carle model 4102). The column configurations for each valve position are shown in Figure 3. The indicated restrictors are adjustable S.S. 1/16" Nupro needle valves and are used to match the pressure drop across various columns as these columns are switched in and out of the flow circuit.

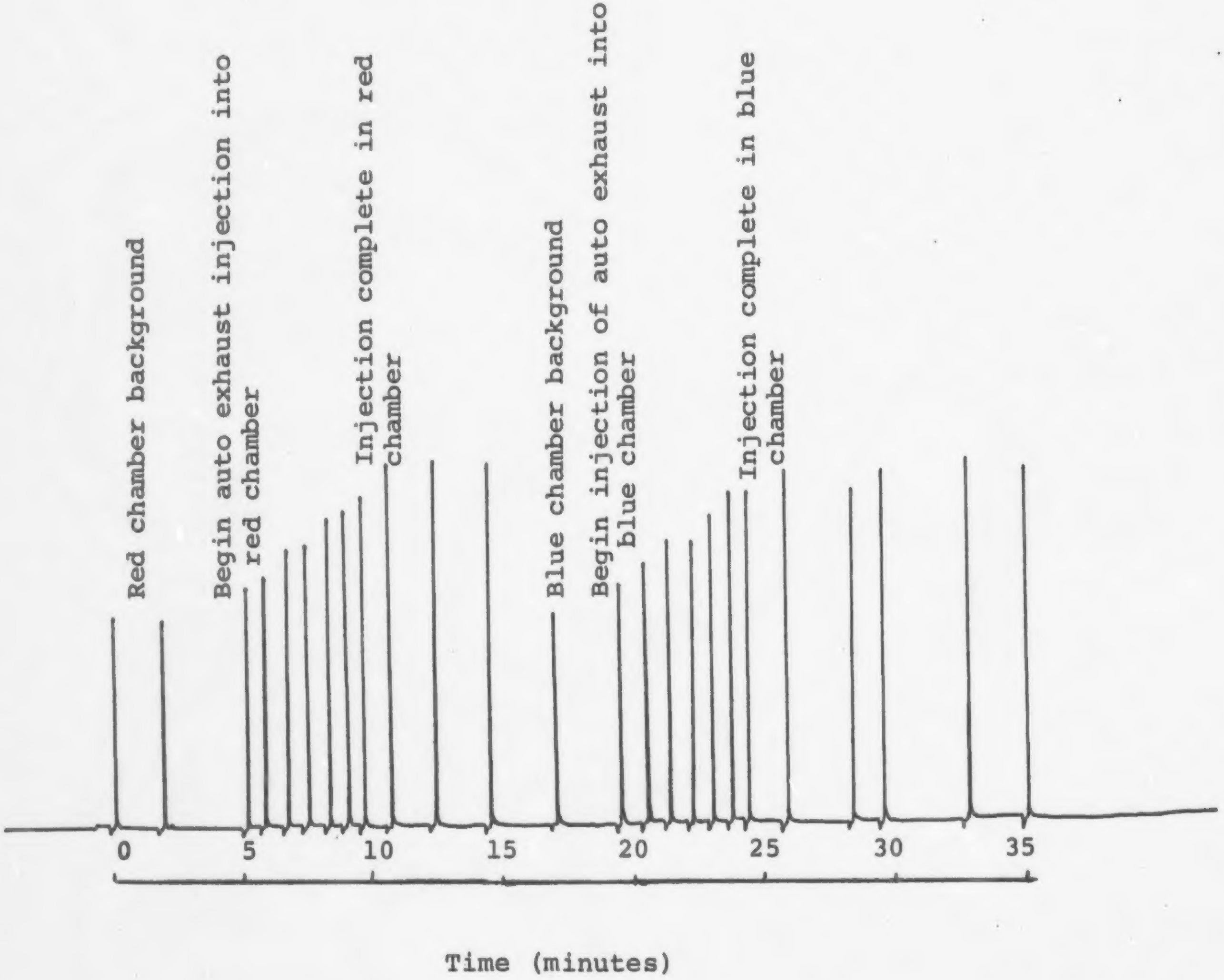


Figure 2. Monitoring of total hydrocarbon concentration as auto exhaust is injected into UNC Outdoor Chambers with a 10 cc direct injection into the flame detector of a Carle I model 211 gas chromatograph.

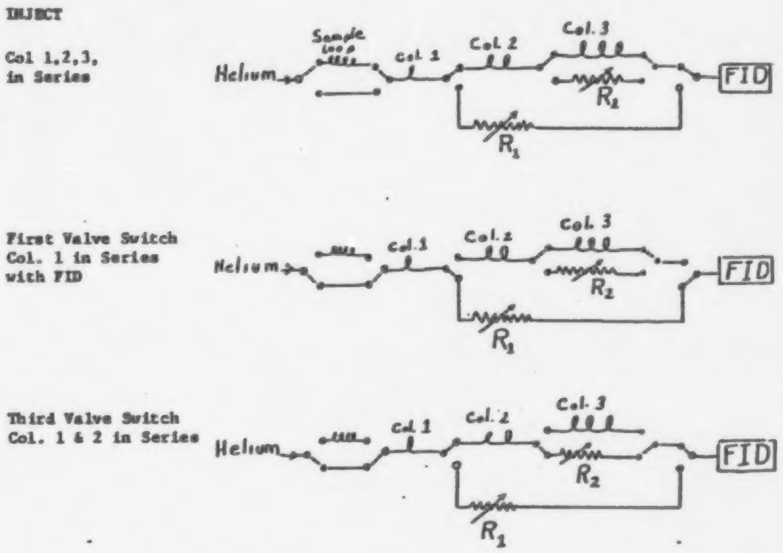

INJECT
Col 1,2,3, in Series
Sample loop
Col 1
Col 2
Col 3
Helium
R2
R1
FID
First Valve Switch Col. 1 in Series with FID
Helium
Col. 1
Col. 2
Col. 3
R2
R1
FID
Third Valve Switch Col. 1 & 2 in Series
Helium
Col 1
Col. 2
Col. 3
R2
R1
FID

Figure 3. Column and Valve Configuration for C_1–C_{10} Automatic Carle Chromatograph.

Automatic injection is made with all three columns in series. One and one half minutes are required for the individual compounds to become distributed into the proper columns. Since column 1 is the first to be encountered, C_6–C_8 are retained, while C_1–C_5 pass on to column 2. After this first 1.5 minutes with the columns in series, a valve switch removes column 2 and 3 from the flow path and permits the compounds in column 1 to elute into the FID. The system remains in this configuration for 5.5 minutes so that C_6–C_{10} paraffins and toluene can be eluted. We also extend this time to 14 minutes to measure xylenes or α-pinene.

A second valve switch then briefly (1 minute) places columns 1, 2, and 3 back in series so that methane and ethylene can be detected. During this period, propane and propylene move from column 2 to column 3 but do not elute before the third valve switch. This switch removes column 3 and leaves columns 1 and 2 in series with the detector. Butenes, pentanes and pentenes then elute from column 2. Finally, with only 2.5 minutes remaining in the cycle, the columns are placed back in series so that propane, propylene and acetylene can be measured.

A chromatogram of the UNC mix is shown in Figure 4. The operating sensitivity can be as low as 7 to 15 ppbC (at a signal to noise ratio of 2 on the most sensitive scale). A limitation of this system is that ethylene and ethane, acetylene and propylene, and some C_4 and C_6 compounds are not completely resolved.

A second packed column GC (Carle II) is used to measure C_1–C_3 hydrocarbons and selected carbonyl species. It employs a 2/'m × 1/8" ss, 60/80 mesh Porapack Q column for C_1–C_3 separation and a 3 m 1/8" SS 10% carbowax 20M (80:100 supelcoport) column for the carbonyls; toluene and xylenes also elute from this column. As with Carle I, Carle II uses the same type motor-actuated valves and a programmable valve controller. A 5-cc air sample is injected onto each column every 15 minutes. While one column is in series with the flame detector, the other is being back flushed. A typical 30 minute analysis on this system is shown in Figure 5.

The third packed column chromatograph (Carle III) is used to resolve C_4 and C_5 hydrocarbons on one column and aromatics on another. It uses a GP 80/100 mesh, Carbopack 19% picric acid, 1/8" SS × 3-m column for C_4 and C_5 and 1/8" × 3-m, GP 10% TCEP, on 100-120 Chromosorb AW column for aromatics. A valve diagram of this system and a chromatographic analysis of automobile exhaust are shown in Figure 6 and Figure 7.

As can be seen, many compounds such as propylene, butenes, toluene and xylenes can be detected by two or even all three of these chromatographs. Most compounds can be quantitatively determined at concentrations of 0.05-0.1 ppmC and, in instances when peaks are sharp, at levels of 0.01 ppmC. The output from each of these instruments is monitored with a Perkin Elmer Sigma 10 integrator and also with stripchart recorders. Since 30 minutes is required for one complete analysis a sample from each chamber side is taken every hour.

Aromatic compounds are detected with greater sensitivity and resolution by two capillary FID gas chromatographs. The first system was built around a Perkin Elmer 900 gas chromatograph and the second uses a Perkin Elmer Sigma 2.

A plumbing diagram for the first system is shown in Figure 8. Programmed signals from the Sigma 10 integrator autoactuate two 6-port, pneumatically operated valves which allow multiple 11-cc samples to be trapped in a freeze-out loop.

CONCENTRATIONS OF INDIVIDUAL SPECIES IN
0.39 PPMC NMHC UNC MIX

	COMPOUND	CONCENTRATION (PPMC)
1	2-METHYLPENTENE	0.035
2	2,4-DIMETHYLPENTENE	0.039
3	2,2,4-TRIMETHYLPENTANE	0.040
4	ETHYLENE	0.042
5	BUTENE-1	0.010
6	BUTENE-2	0.013
7	ISOPENTANE	0.053
8	N-PENTANE	0.092
9	2-METHYLBUTENE-1	0.008
10,	2-METHYLBUTENE-2	0.007
11	PROPYLENE/ACETYLENE	0.047

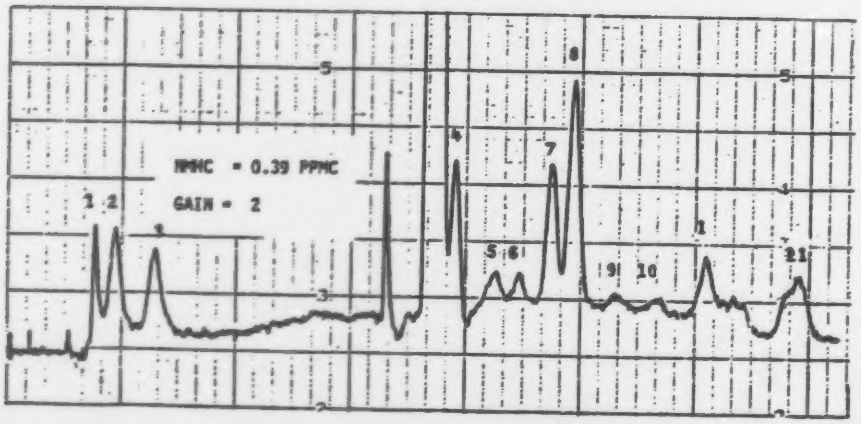


Figure 4. Maximum sensitivity of Carle chromatograph on attenuation of X1 and gain of 2.

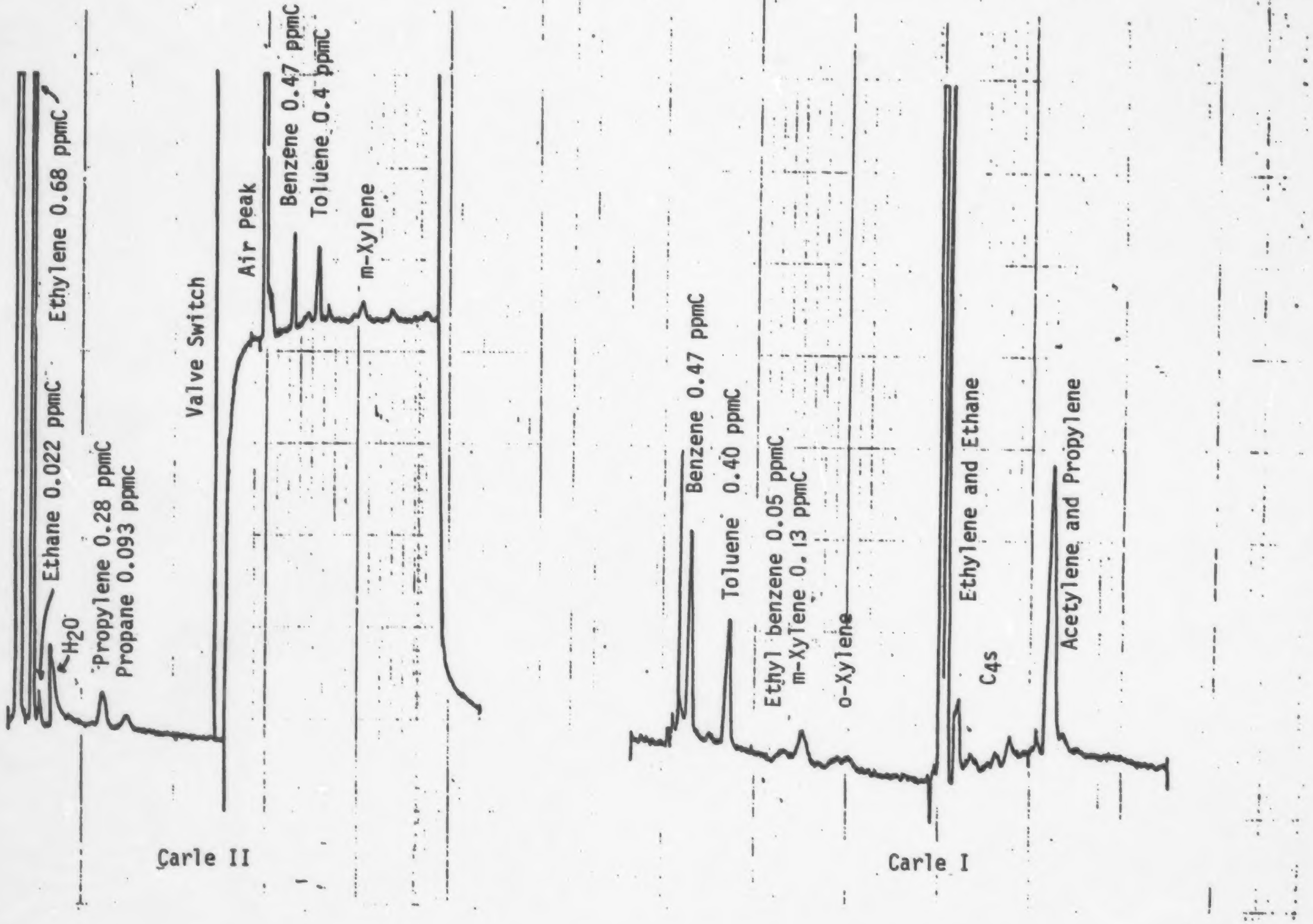


Figure 5. Analysis of C_1-C_8 hydrocarbons in 4 ppmC dilute chamber auto exhaust on Carle II (Model 211) packed column gas chromatograph (July 1, 1982).

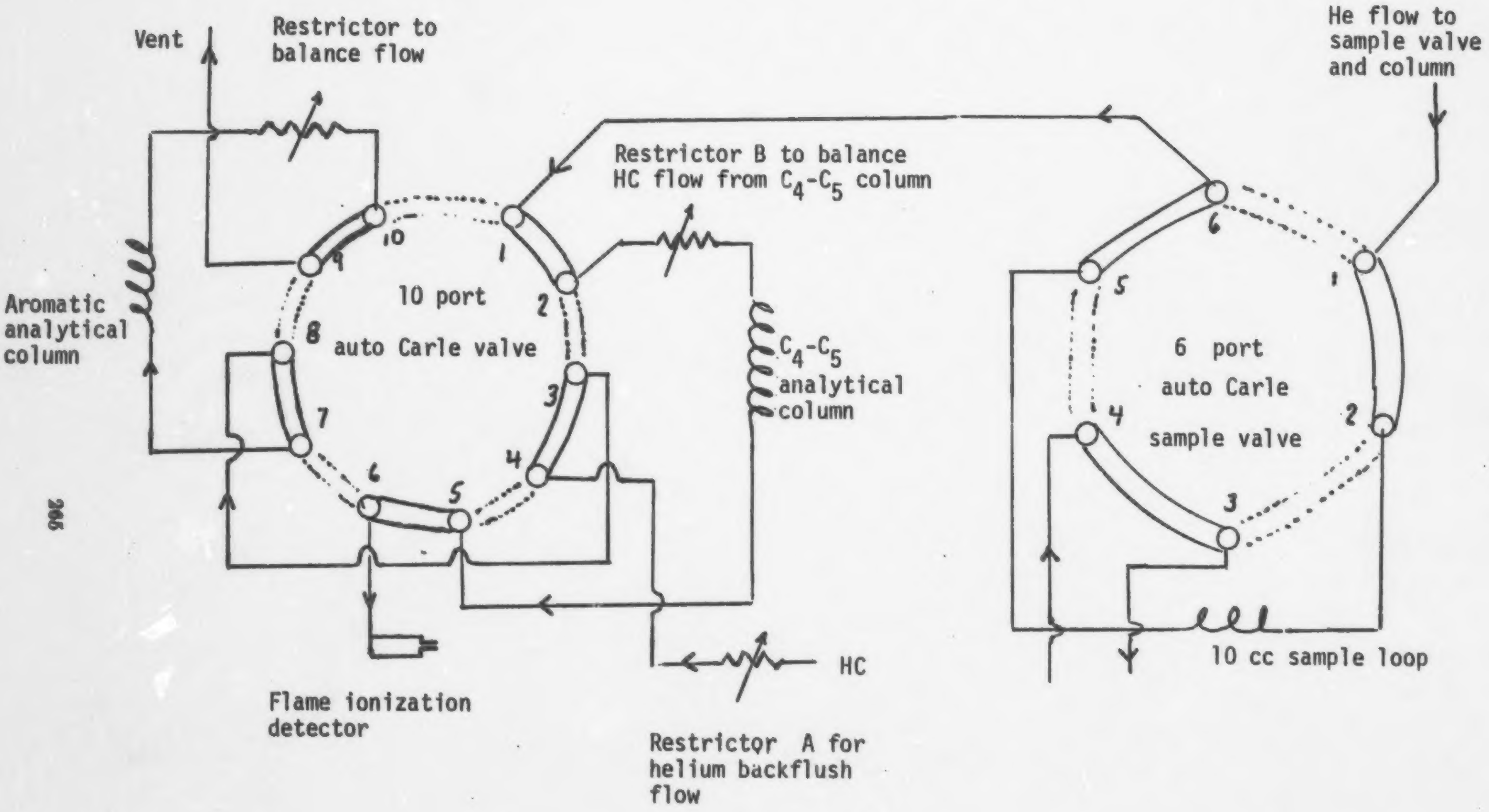

Vent
Restrictor to balance flow
Aromatic analytical column
10 port
auto Carle valve
1
2
3
4
5
6
7
8
9
10
Restrictor B to balance HC flow from C_4-C_5 column
C_4-C_5 analytical column
Flame ionization detector
Restrictor A for helium backflush flow
HC
He flow to sample valve and column
6 port
auto Carle
sample valve
1
2
3
4
5
6
10 cc sample loop

Figure 6. Plumbing diagram to Carle III pack column as chromatograph for the analysis of C_4-C_5 hydrocarbons and aromatic compounds. He flow through columns – 35 cc/min, backflush He – 45 cc/min, restrictions are 1/16" SS needle valves, oven temperature 60°C.

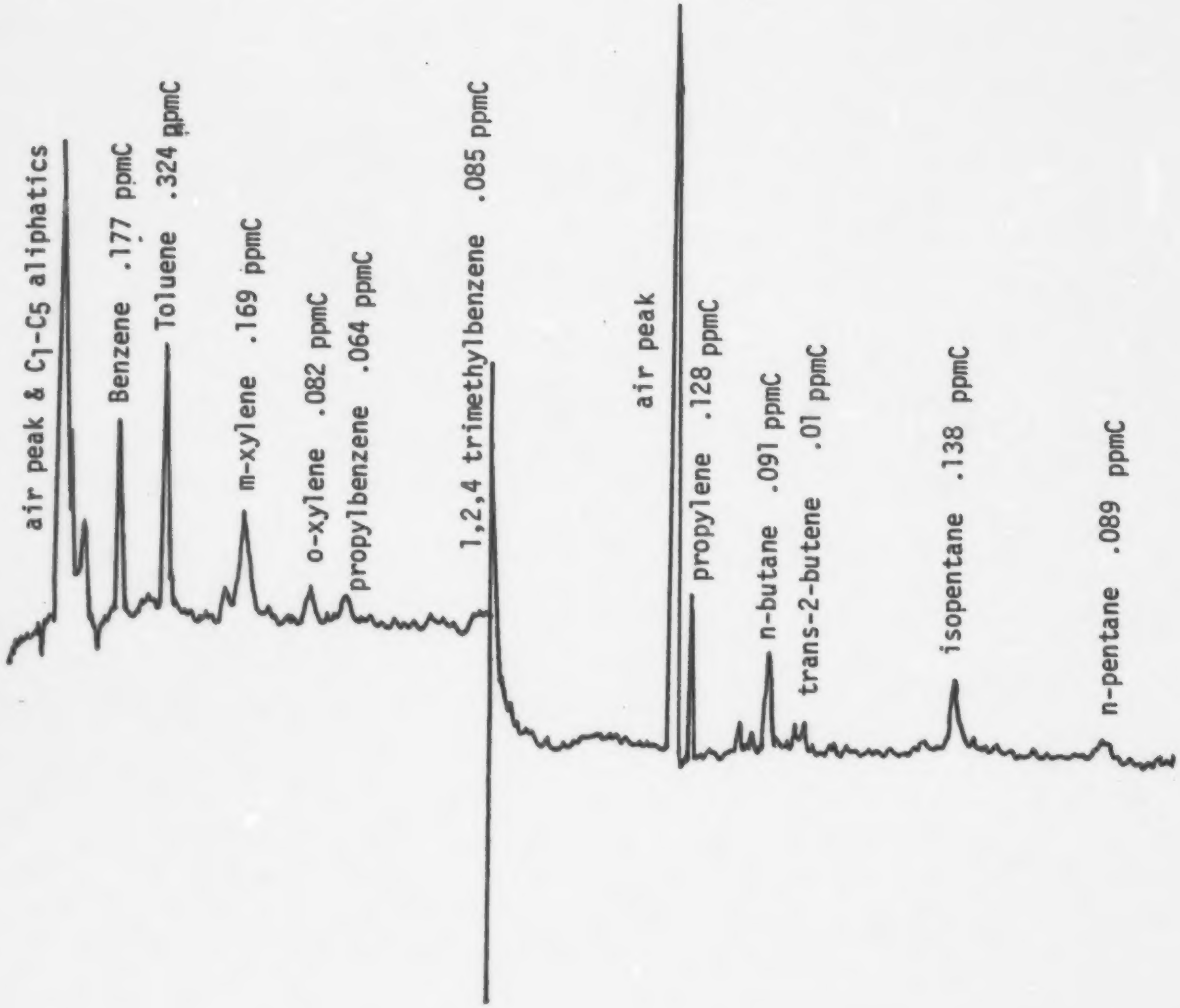


Figure 7. Analysis of aromatics and C_4-C_5 hydrocarbons from dilute auto exhaust injected into UNC outdoor chambers, October 4, 1983.

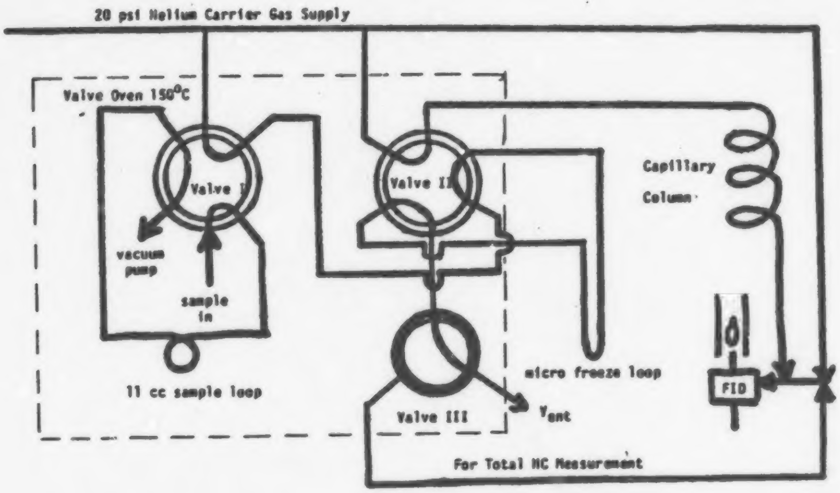

20 psi Helium Carrier Gas Supply
Valve Oven 150°C
Valve I
Valve II
Capillary
Column
vacuum
pump
sample
in
11 cc sample loop
micro freeze loop
FID
Valve III
Vent
For Total HC Measurement

Figure 8. Plumbing Diagram for Perkin Elmer Capillary GC for Aromatic Analysis.

The sample is then automatically desorbed onto a 30 m DB 1 (J & W) or SP2100 (H.P.) fused silica column.

The freeze-out loop has an internal volume of 50 to 150 μliters. It is packed with 60/80 mesh glass beads to increase the internal surface area and decrease the internal dead volume. The effective internal volume is ≈25-75μliters. A dry ice/methanol bath is manually used to cool the trap. The loop is wrapped with fiberglass insulated nichrome wire for the thermal desorption and will heat the loop from liquid nitrogen temperatures to 200°C in less than one minute.

The operating cycle is controlled by a solid state controller. After an initial hold of 6 minutes for valve switching, the column is programmed from 40°C to 150°C at 6.5°C per minute.

This system will separate hydrocarbons from C_6 through C_{14}. A wider range is possible using sub-ambient column temperatures. A typical calibration chromatogram from a mixture of hydrocarbons injected into the chambers is shown in Figure 9 and an analysis of dilute chamber automobile exhaust in Figure 10. Benzaldehyde, tolualdehydes, cresols, nitro benzenes, nitro and toluenes, nitro cresols and dimethyl phenols can also be monitored with this system. The analytical sensitivity of this GC to most compounds is in the 5 ppbC range. A complete analysis requires 45 minutes, including oven cooldown and injection. Thus one sample is taken from each chamber every 1.5 hours.

The fully automated capillary system was designed at UNC around a Perkin Elmer Sigma 2 GC and a Spectra Physics 4100 integrator. A separate controller box was built to drive a LN_2 cryogenic sample concentrator and then thermally degas the trapped HC species onto a 30m DB-1 capillary column. Prior to the start of an analysis the oven is cryogenically cooled with LN_2 to -40°C and then, during the analysis, it is programmed to 180°C; one complete cycle requires 45 minutes and compounds in the C_3–C_{10} range can be analyzed with a sensitivity of 1-3 ppbC. The advantage of this system is its increased sensitivity and the potential to ultimately monitor C_3–C_{12} hydrocarbons in one chromatographic cycle. This permits us to analyze most hydrocarbons on one system and provide better estimates of paraffin to olefin ratios. An example chromatogram of a calibration mixture is shown in Figure 11.

A list of pure compounds and standard mixtures used to calibrate this gas chromatograph is given in Table 4.

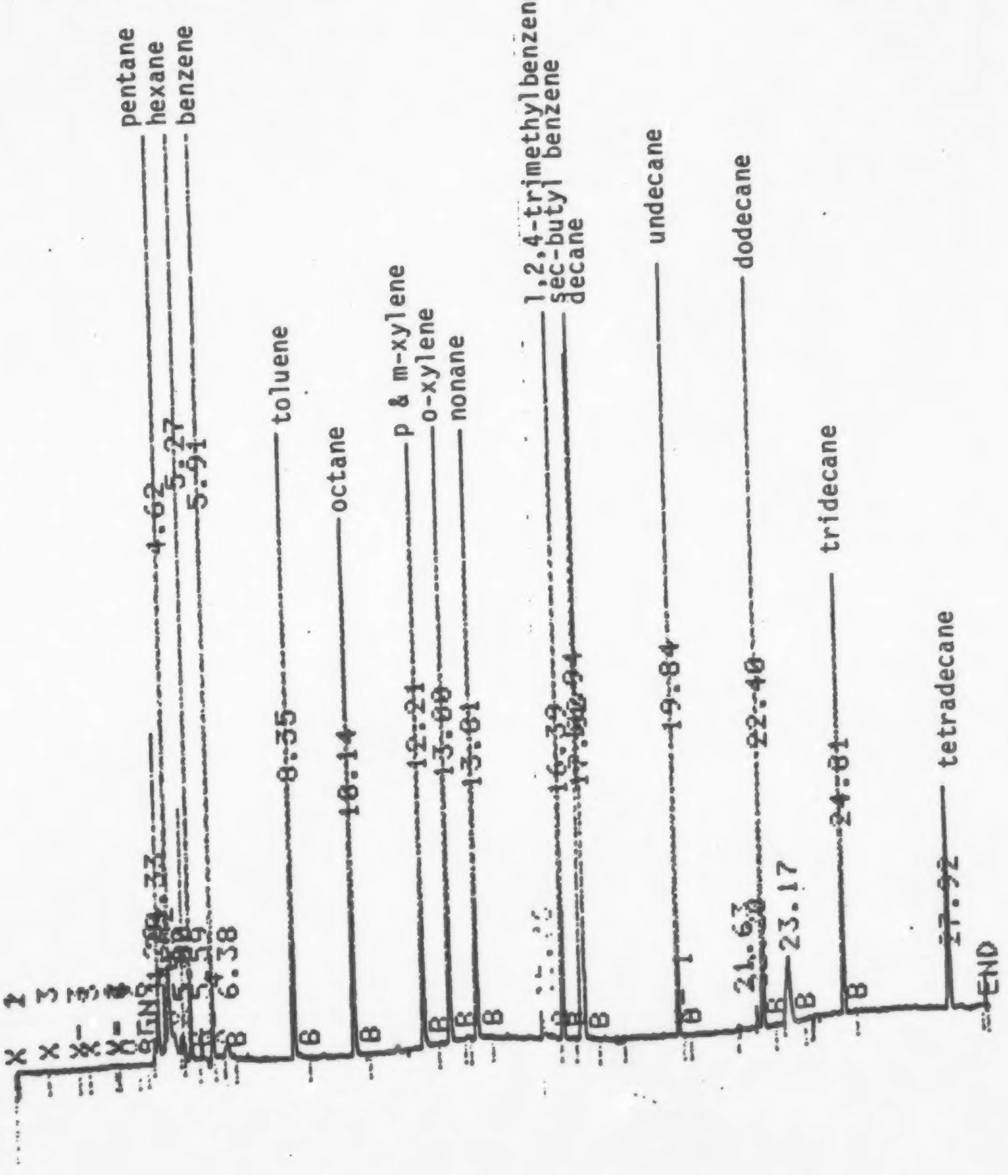


Figure 9. Calibration Chromatogram on PE 900 FID Gas Chromatograph 30 m DB-1 fused silica column (J&W), 22 cc air sample concentrated in 1/16" × 8" SS tube packed with 60/80 mesh glass beads (internal volume 25-75 ul) cooled with MeOH dry ice and thermally desorbed at 200°C with heat tape. Initial oven temperature = 40°C and programmed at 6.5°C/min to 150°C.

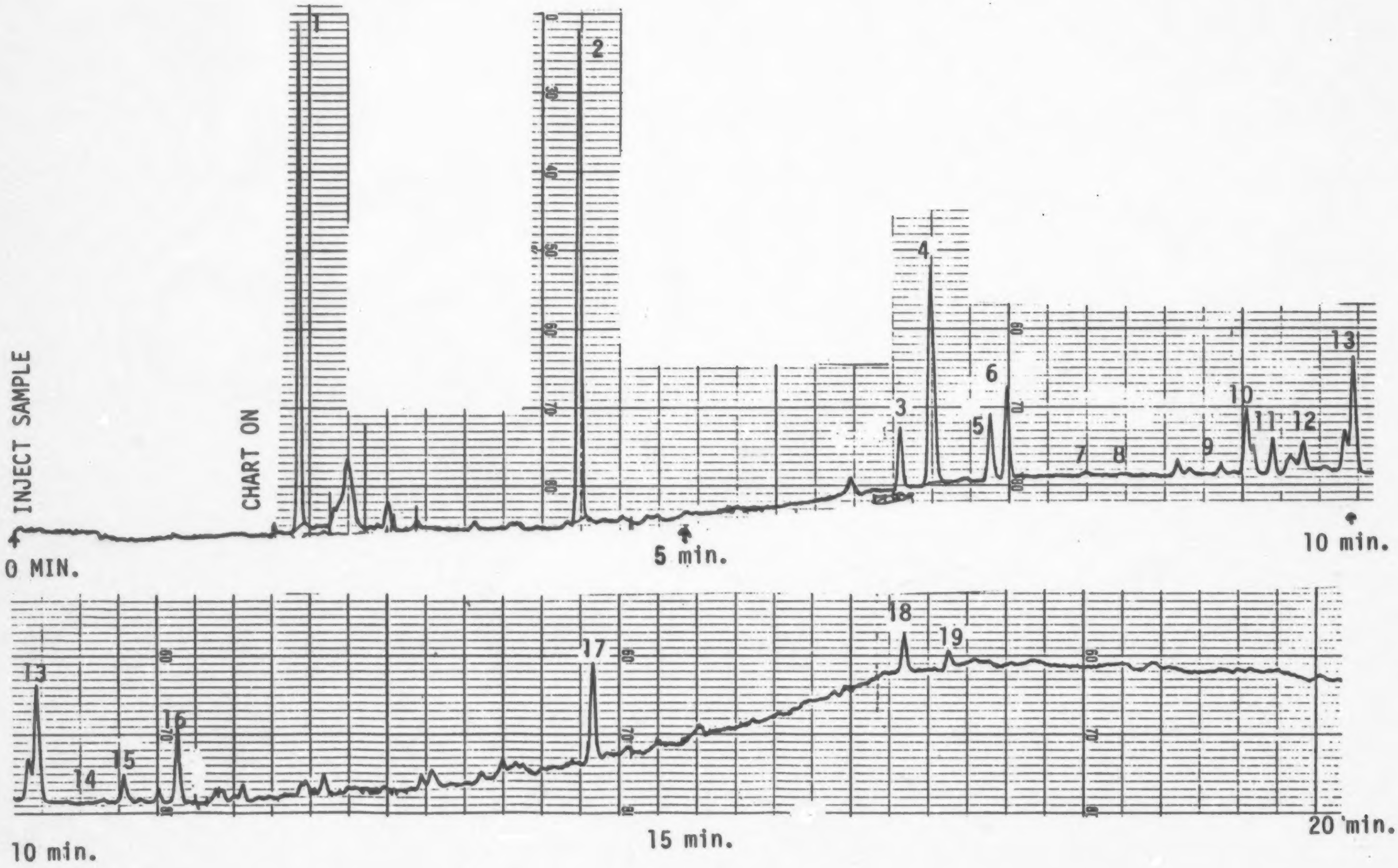


Figure 10. Analysis of C_6C_{12} aromatics on PE 900 FID capillary gas chromatograph from a 3 ppmC dilute auto exhaust chamber run on June 30, 1982. Compound identities and concentrations are: 1) benzene, 0.337 ppmC 2) toluene, 0.366 ppmC 3) ethylbenzene, 0.051 ppmC 4) m&p-xylene, 0.187 ppmC 5) styrene, 0.059 ppmC 6) o-xylene, 0.078 ppmC 7) nonane 8) isopropylbenzene 9) n-propylbenzene, 0.012 ppmC 10) m-ethyltoluene, 0.057 ppmC 11) 1, 3,5-trimethylbenzene, 0.032 ppmC 12) o-ethyltoluene, 0.017 ppmC 13) 1,2,4 trimethylbenzene + tert-butylbenzene, 0.097 ppmC 14) decane + secbutylbenzene 15) 1,2,3 trimethylbenzene, 0.019 ppmC 16) dimethylethylbenzene, 0.062 ppmC 17) napthylene, 0.083 ppmC 18) 2-methylnapthylene, 0.0313 ppmC 19) 1-methylnapthylene, 0.015 ppmC.

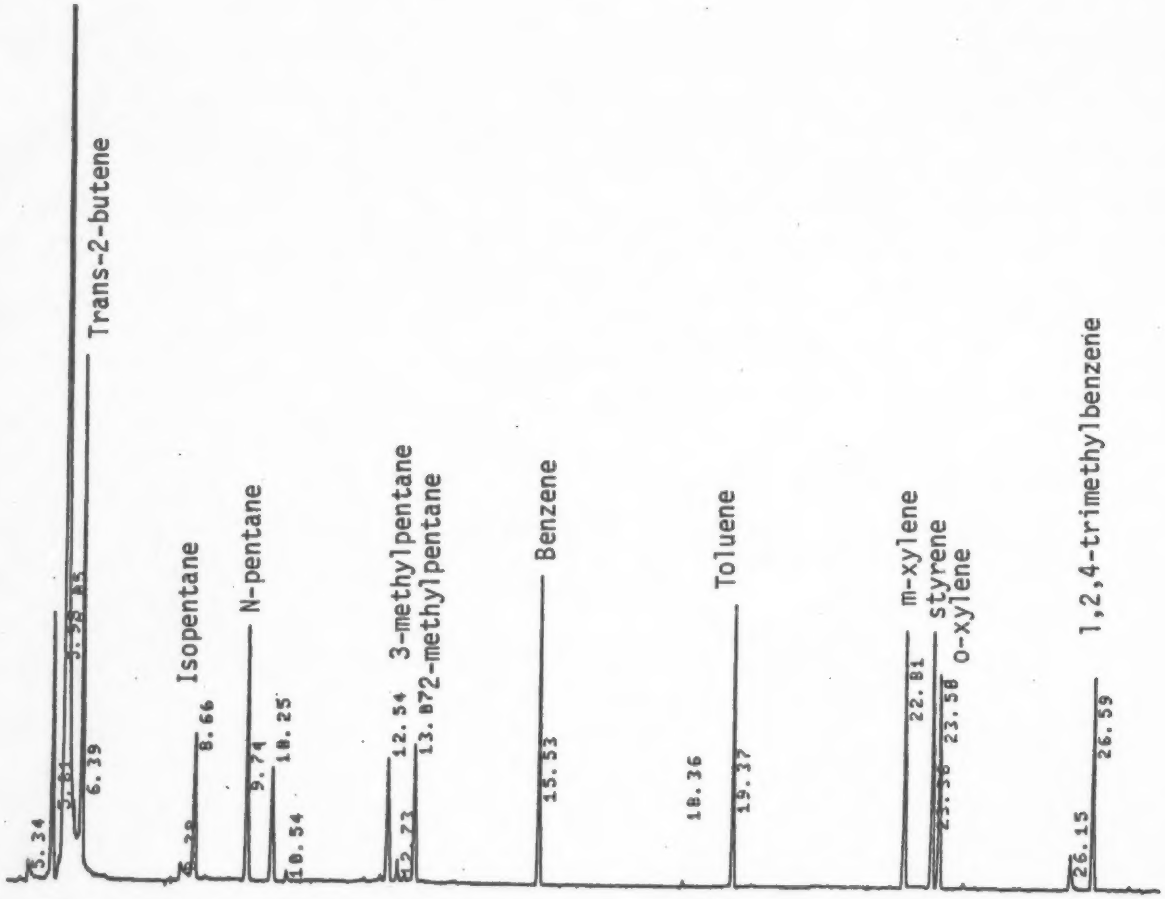


Figure 11. Chromatograph of calibration mixture on auto sampling Perkin Elmer Sigma 2 capillary gas chromatograph with 30 m DB-1 column (J&W). 30 cc air sample (with 0.5 ppmC of each alkane and 1 ppmC of each aromatic) to auto LN_2 trap, oven = -40°C hold (5 min hold) program rate 5°C/min to 150°C, final hold 5 min. Signal attenuated 10 fold.

Table 4 Species Use for Identification and Calibration on PE Sigma 2

Species	Source
propylene	1
propane	1
propadiene	1
butane	1
isobutane	2
1-butene	1
1,3-budtadiene	1,6
cis-2-butene	1
trans-2-butene	1
2-me-1,3-butadiene	1
2-methylpropene	5a,6
2-methyl-1-butene	3
2-methyl-2-butene	3
isopentane	1
n-pentane	1
1-pentene	2
cyclopentene	4
2,2-dimethylpropane	5a,6
benzene	2
2-methylpentane	2
3-methylpentane	4
2-methyl-1-pentene	5a,6
4-methyl-1-pentene	5a,6
cyclohexene	4
cyclohexane	2
n-hexane	2
n-heptane	2
2,3-dimethylpentane	2
3-methylhexane	5a

Table 4 Species Used for Identification, continued

Species	Source
toluene	2
methylcyclohexane	4
n-octane	1
m-xylene	2
o-xylene	2
styrene	4
ethylbenzene	2
o-ethyltoluene	4
m-ethyltoluene	4
1,2,3-trimethylbenzene	4
1,2,4-trimethylbenzene	4
1,3,5-trimethylbenzene	4
n-propylbenzene	4
isopropylbenzene	4
n-butylbenzene	4
s-butylbenzene	4
t-butylbenzene	4
diethylbenzene	5b
dimethylethylbenzene	4
naphthalene	5b
1-methylnaphthalene	4
2-methylnaphthalene	4

1 Certified Cal. tank, LOMW
2 Certified Cal. tank, HIMW
3 Calibrated Injection tank, UNCMIX
4 UNC General Chemical Supply
5a Mobile Sources Emissions Research Branch, EPA
5b Mobile Sources Measurements Research Section, EPA
6 William Lonneman, Gas Kinetics and Photochemistry Branch, EPA

Mass Spectrometry

Individual identification of hydrocarbon species in mixtures as complex as automobile exhaust is performed at UNC on a VG micro-mass 707F mass spectrometer interfaced to a Hewlett Packard 5710A capillary gas chromatograph. One to two cc of raw automobile exhaust are injected onto a 30 m, SE54, or DB-1 fused silica column. The first 0.3 meters of the column are coiled into a cup of liquid nitrogen so that on-column trapping of the sample can be accomplished. The oven is then programmed from 10°C to 150°C at 5°C/min. Identification is performed by comparison to the mass spectrum from authentic samples and to literature spectra available in the EPA-NIEHS mass spectra libraries. An analysis of raw automobile exhaust and gasoline is shown in the reconstructed ion chromatographs in Figure 12 and Figure 13. Figure 14 is a library mass spectrogram of napthalene and Figure 15 is the mass spectrogram of peak 43 in Figure 12, and there is little doubt that peak 43 is napthalene.

Quantification of individual hydrocarbon species is performed on an "off line" Carlo Erba 4130 FID gas chromatograph. The same fused silica column, cryotrap and temperature program which were used for the GCMS analysis are used here. Identifications are made by comparing the FID chromatogram (Figure 16) with the GCMS reconstructed ion chromatograms. Response factors are determined from a mixture of 15 authentic compounds which are analyzed on the Carlo Erba.

Formaldehyde by Automated Colorimetry

Since 1979, UNC has used an automated colorimetric formaldehyde instrument manufactured by CEA corporation (Westwood, NJ). This system employs a reverse West and Gaeke technique[1] and hence requires a constant supply of wet chemicals which include highly purified pararosanaline, mercuric chloride, sodium chloride, and sodium sulfite.

Liquid standards are prepared from 37% formalin solution and diluted in the same sodium tetra mecurate (TMC) used in the instrument. A dynamically generated HCHO airstream using a formaldehyde permeation tube (Metronics Corporation, Santa Clara, CA) is used to supply known levels of gas phase formaldehyde. In addition, calibration samples of formaldehyde are prepared in the chamber. The chamber is usually dried to a dew point of less than 60°F and known quantities of solid paraformaldehyde are then injected. During the course of a six month data

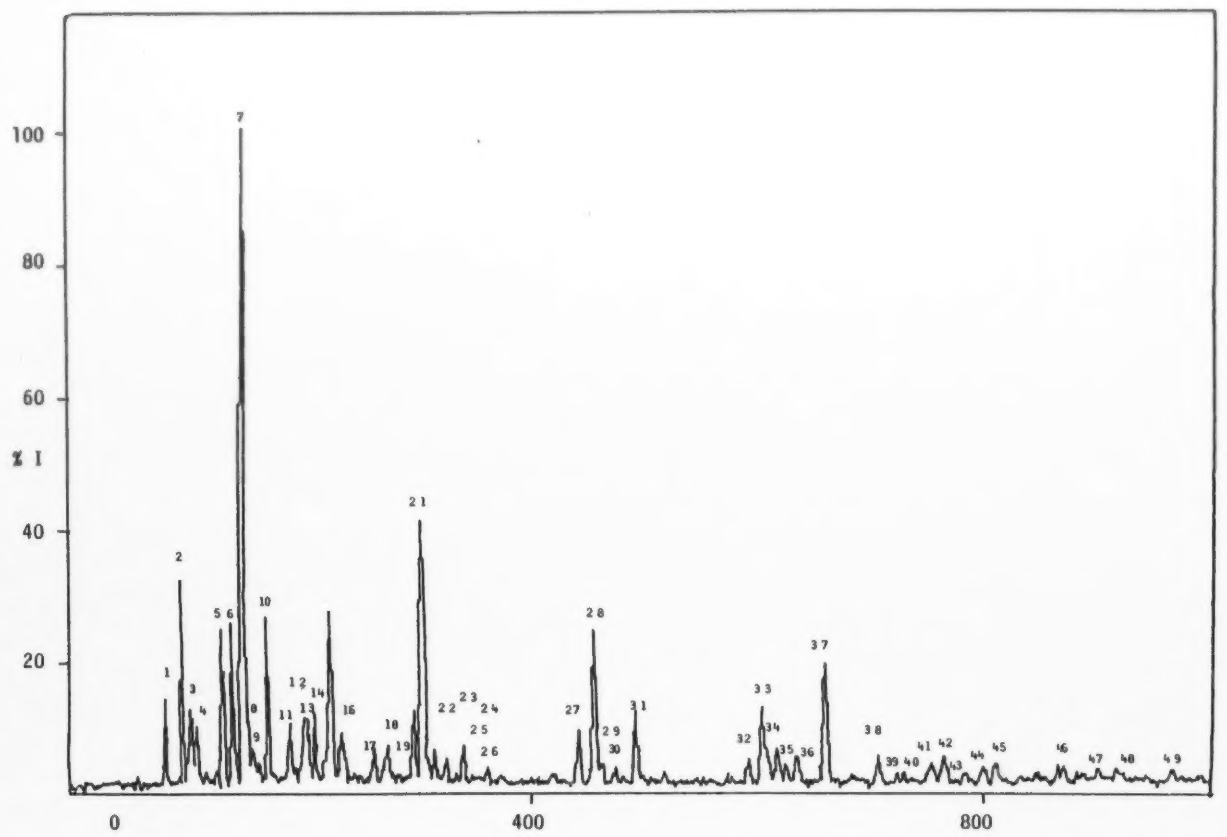


Figure 12. Reconstructed ion chromatograph of EPA summer gasoline using DB-1 column. Identities based on comparison with literature mass spectra. Compounds listed in order of elution are: 1) n-butane 2) 2-methylbutane 3) n-pentane 4) methylbutene or 2-pentane 5) 2-methylpentane 6) 3-methylpentane 7) n-hexane 8) hexadiene or a methylcyclopentene + a hexene 9) e-methyl-2-pentene 10) methylcyclopentane 11) benzene 12) 2- methylhexane 13) 2,3-dimethylpentane 14) 3-methylhexane 15) 2, 2,4-trimethylpentane 16) n-heptane 17) methylcyclohexane 18) 2 ,5-dimethylhexane 19) 2,4-dimethylhexane 20) 2,3,4- trimethylpentane or 4-methylheptane 21) toulene 22) 2,3- dimethylhexane 23) 2-methylheptane 24) 3-methylheptane 25) 2,2 ,4- or 2,2,5-trimethylhexane 26) n-octane 27) ethylbenzene 28) m- and/or p-xylenes 29) methylpentanes 30) 3-ethylheptane 31) xylene 32) n-propylbenzene 33) m- and/or p-ethyltolune 34) 1,3 ,5-trimethylbenzene 35) 2- or 4-methylnonane 36) p-ethyltoluene 37) 1,2,4-brimethylbenzene 38) 1,2,3-trimethylbenzene 39) n- decane and other C_10 alkylbenzene 40) indan or a methylstyrene 41) sec-butylbenzene and other C_4 alkylbenzene (m-tp-n-propyltoluenes and maybe some tert–butylbenzene) 42) n- butylbenzene and other C_4 alkylbenzene (maybe some diethylbenzenes) 43) n-propyltoluene and some undecane 44) dimethylethylbenzenes 45) a dimethylethylbenzene 46) tetramethylethylbenzenes 47) C_5 alkylbenzene and C_4 alkenebenzene 48) C_4 alkenebenzene 49) naphthalene.

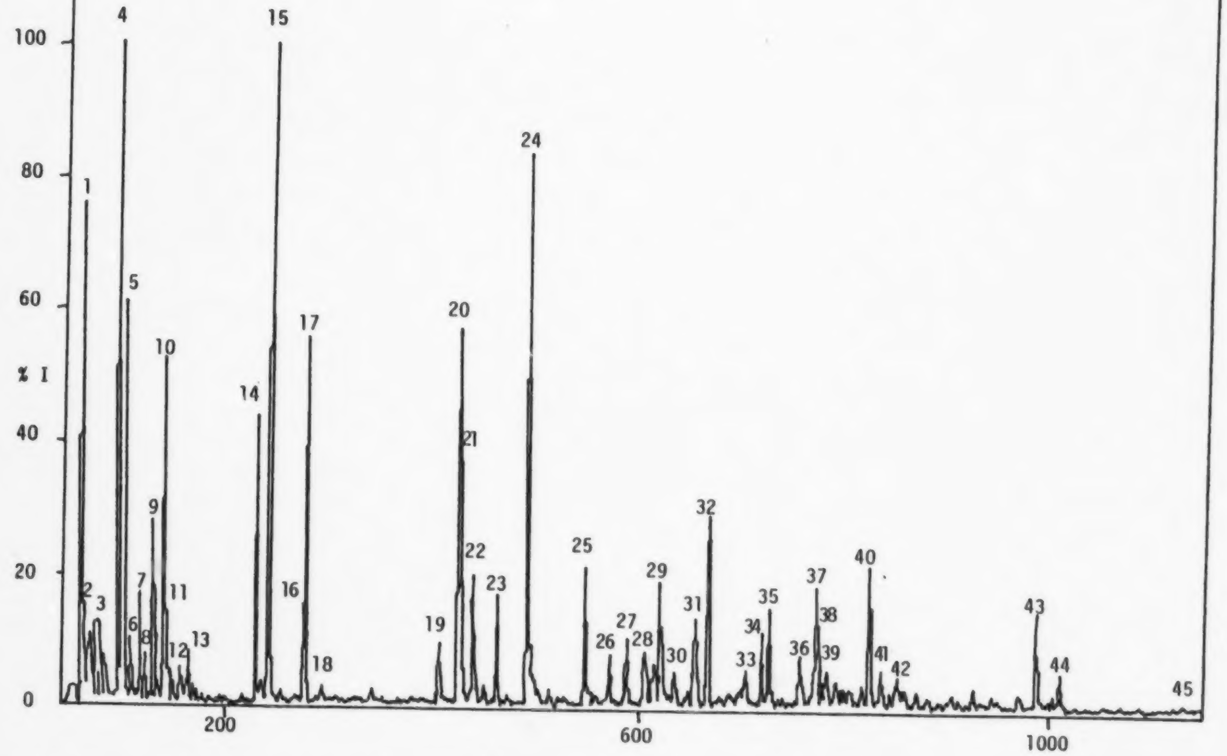


Figure 13. Reconstructed ion chromatograph of 1972 Dodge Charger exhaust, running 2200 rpm, using EPA summer gasoline, with 30 m SE54 column. Identities based on comparison with literature mass spectra, compounds listed in order of elution are: 1) butadiene and a butene or cycle-butane 2) 2-methylbutane 3) a pentadiene, or methylbutene; cyclopentadiene, 2-methylpentane, several hexenes; methylcyclopentane 4) benzene 5) 2,2,3 or 2,2,4- trimethylpentane 6) n-heptane + heptene + heptadiene 7) methylcyclohexane 8) 2,4-dimethylhexane 9) a trimethylcyclopentane then 2,3,3-trimethylpentane and 2,3- dimethylhexane 10) toluene 11) 3-methylheptane then 2,2,4- or 2, 2,5-trimethylhexane or 2,2-dimethylheptane 12) 2-ethyl-1-hexane 13) n-octane + trace of an octene 14) ethylbenzene 15) m- and p-xylenes 16) styrene 17) o-xylene 18) isopropylbenzene 19) n -propyl-benzene 20) m-ethyltoluene 21) p-ethyltoluene 22) 1,3, 5-trimethylbenzene 23) o-ethyltoluene 24) 1,2,4- trimethylbenzene and small amount of methylstyrene or indan 25) 1,2,3-trimethylbenzene 26) indan or a methylstyrene 27) indene 28) sec-butylbenzene and some m & p-n,propyl-toluene and maybe some t-butylbenzene; then n-propyltoluene; then n-butylbenzene and some diethylbenzene 29) a dimethylethylbenzene 30) po-n, propyltoluene 31) a dimethylethylbenzene 32) a dimethylethylbenzene and trace C_4 alkenebenzene 37) a C_4 ene and a C_5 alkylbenzene 38) a tetramethylbenzene 39) a C_5 alkylbenzene 40) naphthalene 41) a C_5 alkenebenzene 42) a pentylbenzene 43) 2-methylnaphthalene 44) 1- methylnaphthalene 45) a dimethyl-naphthalene

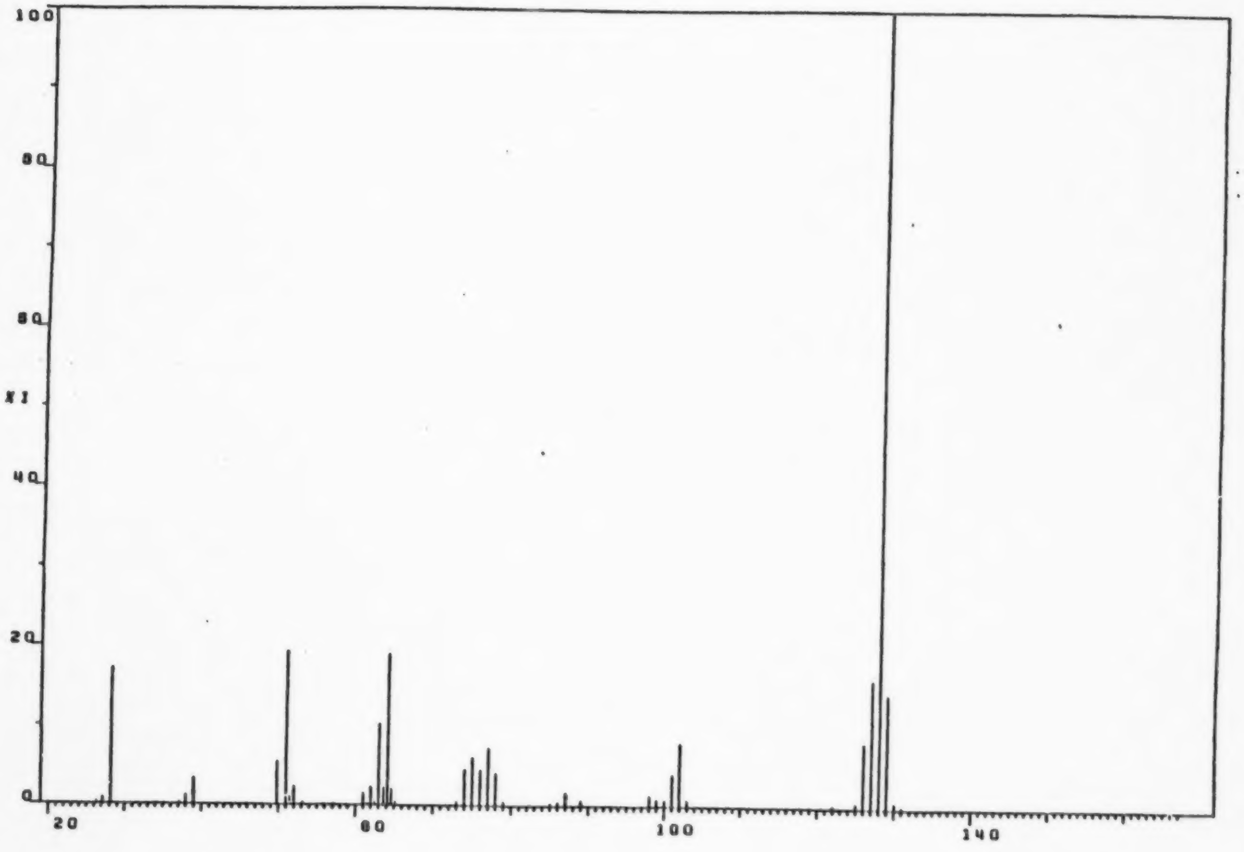


Figure 14. Library mass spectrogram of Naphthalene on the VG Micro-Mass 707F Mass Spectrometer.

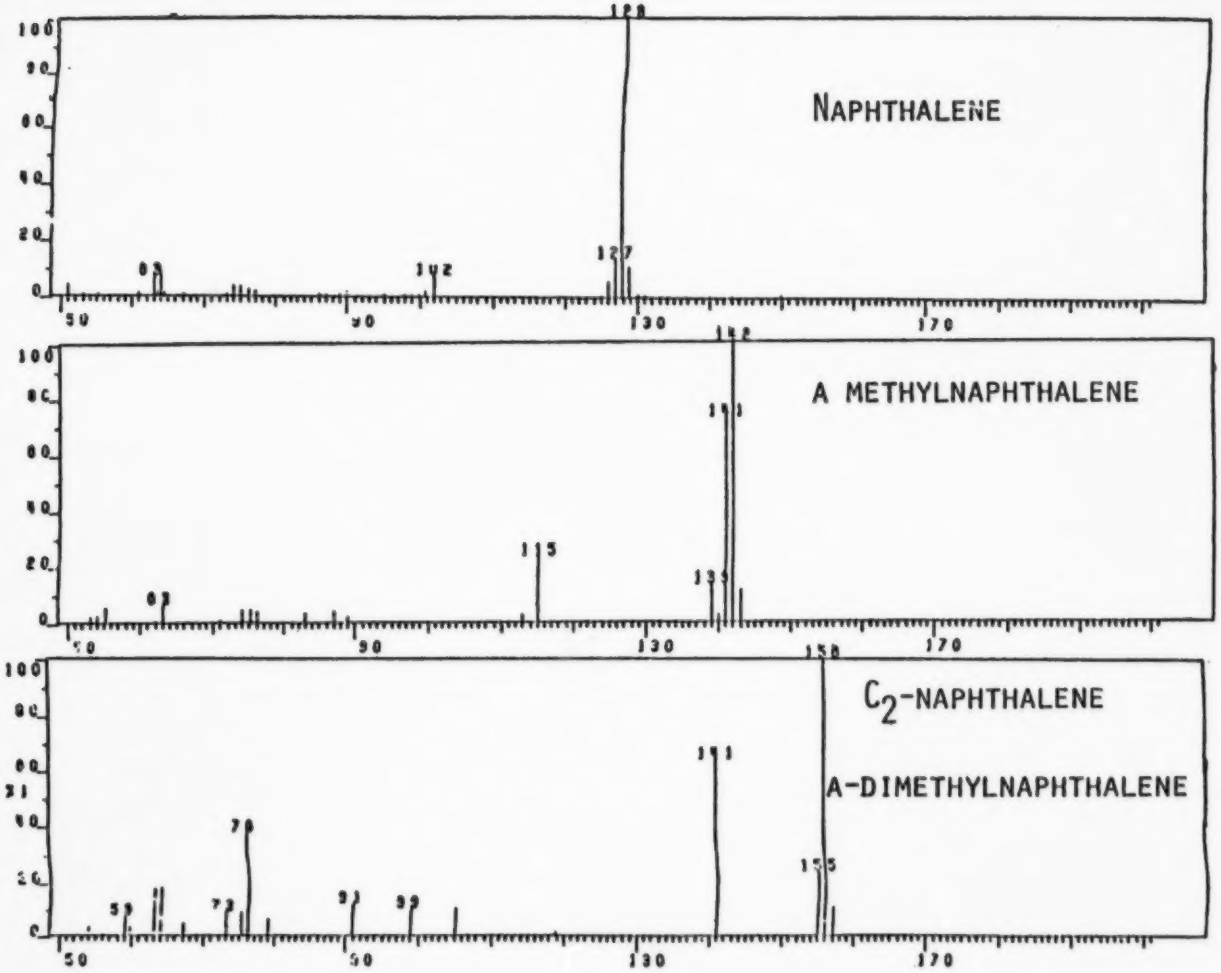


Figure 15. Mass spectrograms of Peaks 43, 44, and 45 of Figure 12, Auto Exhaust.

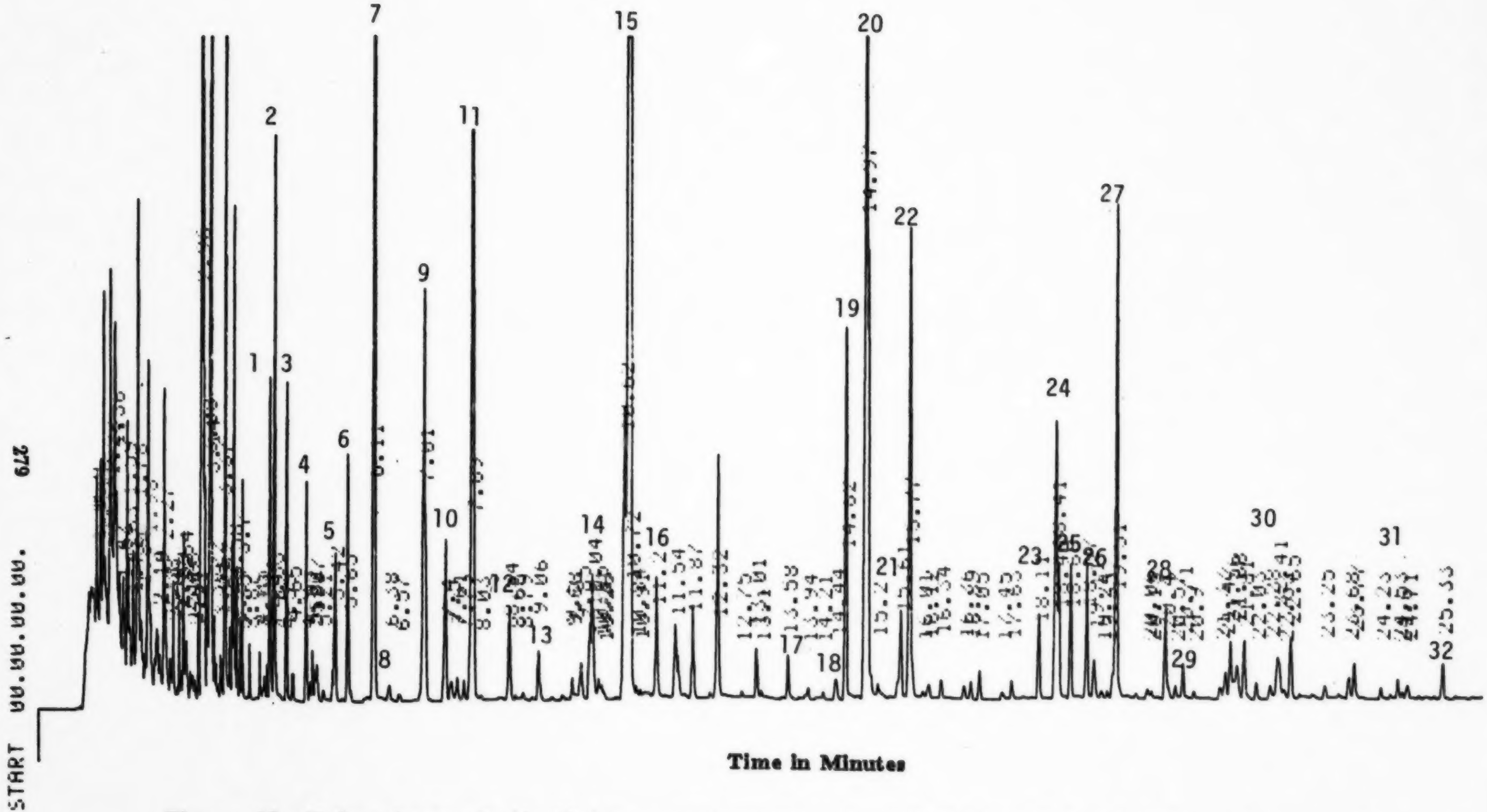


Figure 16. Hydrocarbon species identified in cryocondenser auto exhaust (7-28-83) on Carlo Erba-FID gas chromatograph 30 m DB-1 column (J&W) on column liquid oxygen freeze out. Temperature programmed 10°C hold 7 minutes program at 5°C/min to 150°C. Identities bases on comparison with reconstructed ion chromatographs generated under similar operating conditions. 1) 2,3-dimethylbutane 2) 2-methylpentane 3) 3-methylpentane 4) n- hexane 5) methylcyclopentane 6) 2,2- and/or 2,4-dimethylpentane 7) benzene and some methylcyclopentene 8) cyclohexane 9) 2- methvlhexane 10) 3-methylhexane 11) 2,2,4-trimethylpentane 12) n-heptane 13) methylcyclohexane 14) 2,4-dimethylhexane 15) toluene 16) 2,3-dimethylhexane 17) n-octane 18) 2,5- dimethylheptane 19) ethylbenzene 20) m-& p-xylene 21) 3- methyloctane 22) o-xyiene 23) n-propylbenzane 24) m-& p- ethyltoluene 25) 1,3,5-trimethylbenzene 26) o-ethyltoluene 27) 1,2,4-trimethylbenzene 28) 1,2,3-trimethylbenzene 29) indan 30) C_4-benzene 31) methylindans 32) naphthalene.

season when the chambers are in operation, we have found this system's calibration not to change by more than 10%.

The minimum detectable concentration for this instrument is 20 ppb and a continuous sample on each chamber is taken every 30 minutes. Using the solutions recommended by CEA we observed a 5% positive interference from acetaldehyde in the concentration range of 0.1–1 ppmV. When appreciable acetaldehyde is generated, the HCHO data are adjusted to subtract out the positive acetaldehyde interference. Interferences from other carbonyls such as acetone, propionaldehyde, MEK or methacrolein produced are not significant. Finally, the system that we have been using exhibits a 30-50% zero drift over a 3-4 hour period. This drift does not affect the span response but requires frequent zero samples. Examples of the system's response to 1.2 and 0.5 ppmC formaldehyde air samples are shown in Figure 17.

Carbonyl Analysis

The analysis of C_1–C_8 carbonyl species in ambient air by reaction with 2,4 dinitrophenylhydrazone (DNPH) and subsequent reverse phase high pressure liquid chromatography of the hydrazone derivatives has been reported by Kuwata *et al.*[2] This procedure is fairly specific and can also be used to measure dicarbonyls. We have used this method to monitor C_2 and greater carbonyls and have generally used the previously described automated colorimetry method to obtain more continuous formaldehyde measurements.

Ambient aldehydes are sampled with an impinger arrangement into an absorbing reagent which contains acidified DNPH. Three to four recrystallizations of the DNPH (Eastman Kodak cat. no. 1866, 10% water added) with acetonitrile (ACN) are required to remove impurities from the DNPH. The absorbing reagent is prepared by dissolving 0.25 g of purified DNPH in one liter of HPLC grade ACN. This is followed by the addition of 0.2 ml of H_2SO_4. Two ml of absorbing reagent are used in a Mae West type bubbler with a sample flow rate of one l/min, as described by Kuntz *et al.*[3]. We have observed collection efficiencies of 75–85% for most of the carbonyl compounds which have been tested. These include formaldehyde, acetaldehyde, propionaldehyde, methylvinylketone, benzaldehyde, glyoxal, methylglyoxal, biacetyl and o-tolualdehyde.

Analysis is performed on a Varian 5010 HPLC with a Varian micropak MCH-10 reverse phase, 30 cm, 9 mm column and a fixed 254 nm detector. To eliminate

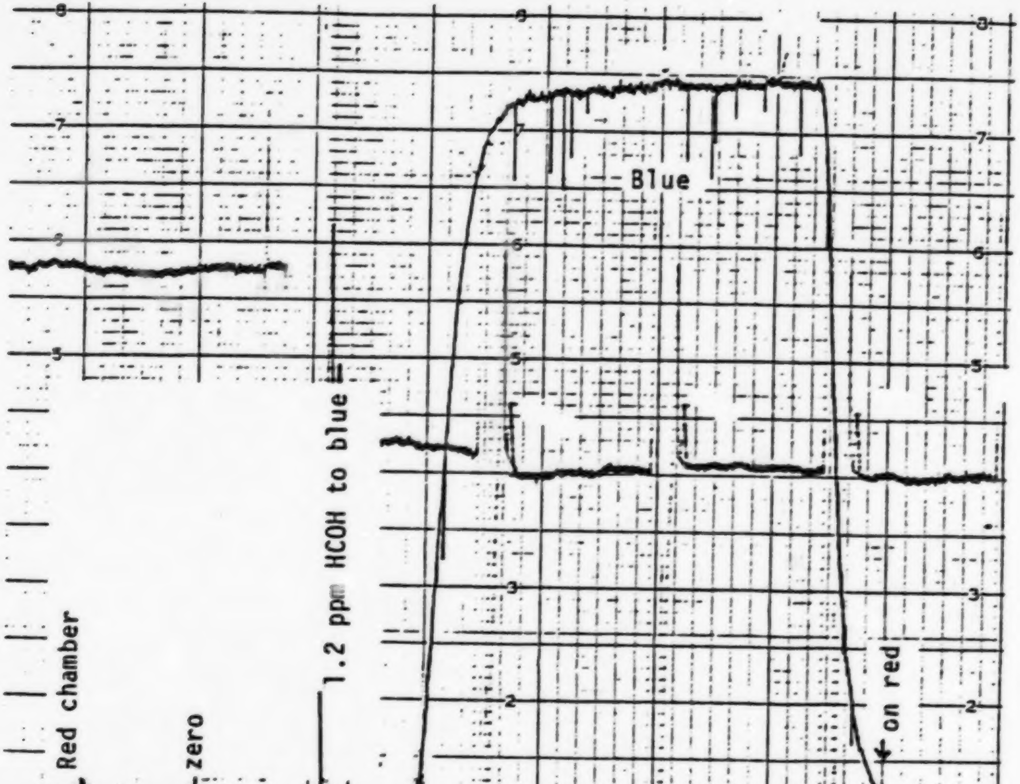


Figure 17. Response of CEA Auto Formaldehyde Instrument to 0.5 and 1.2 ppm of HCOH injected in dry UNC chambers on August 4, 1979 and August 5, 1979.

interferences from toluene and xylenes a 365 nm cut off filter can be used. The mobile phase is run isocratically at a 60:40 ACN:H_2O mixture and a solution flow of 1.6 ml/min. High concentration liquid standards in the gas phase equivalent range of 2-6 ppmV were prepared by direct dilution of 5 μl of authentic knowns (liquids available from Aldrich or Eastman, purity 98–99%, except for 40% gloxal in water, 40% methylglyoxal, 37% formaldehyde, 85% methacrolein and 95% biacetyl. These standards were used as received and not further purified.) to twenty μl of this solution were then added to 2 ml of DNPH absorbing reagent. The final DNPH samples were heated in 2 ml Supelco reaction vials at 70°C for 30 minutes. Comparisons with gas phase and liquid calibration samples are made. A sample chromatogram of a mixture of aldehydes, ketones and dicarbonyls is shown in Figure 18.

PAN Analysis

PAN measurements are made on a 1/8" × 36" glass column packed with 10% Carbowax 600 on Gaschrom G (60-80 mesh) and detected with a Varian 940 electron capture detector. Both the column and the detector are held at room temperature and 5% methane-argon is used as the carrier gas. A 6-port automatic sample valve was installed so that unattended sample injection and analysis could be performed. With a standing current of 20×10^{-9} amps we found that the response was linearly between 0.01 ppmV and 0.5 ppmV of PAN. The response of this system to 0.12 ppmV of PAN is shown in Figure 19.

PAN calibration samples are prepared from an irradiated 5ppmC biacetyl/NO_x bag system. The bag is irradiated for 1 hour in midday sun so that essentially all of the NO_2 is converted to PAN. The PAN is purified with a 10% Carbowax 600 prep-column (25 cm × 7 mm) and a liquid nitrogen freeze-out concentrator. PAN from the cryotrap is then diluted into a clean Teflon bag and measured with a calibrated chemiluminescence NO_x analyzer. The response of the chemiluminescent monitor to PAN is 100% and thus a pure PAN sample can be standardized.

When the above procedure is not possible, then 4 ppmC of propylene and 0.5 ppm NO_x (40% NO_2) are irradiated outdoors for 3-4 hours during the mid-morning and the early afternoon. With a chemiluminescent NO_x meter, the NO_2 concentration is followed beyond the NO_2 peak until NO_2 stabilizes. The PAN GC responses are then related to chemiluminescent PAN readings assuming that all NO_2 that is reported by the meter is actually PAN.

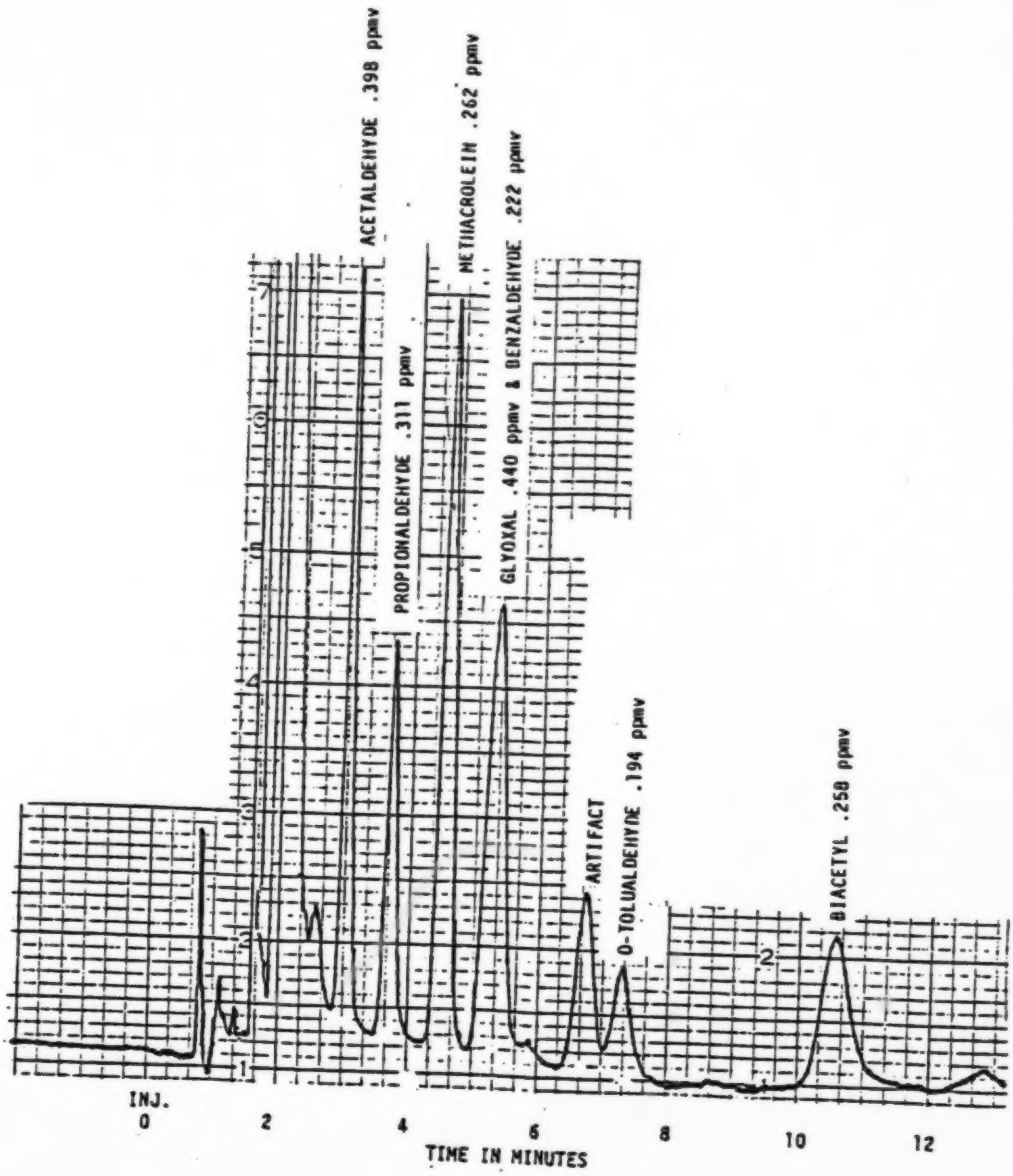


Figure 18. An example of the response of the HPLC with DNPH Method.

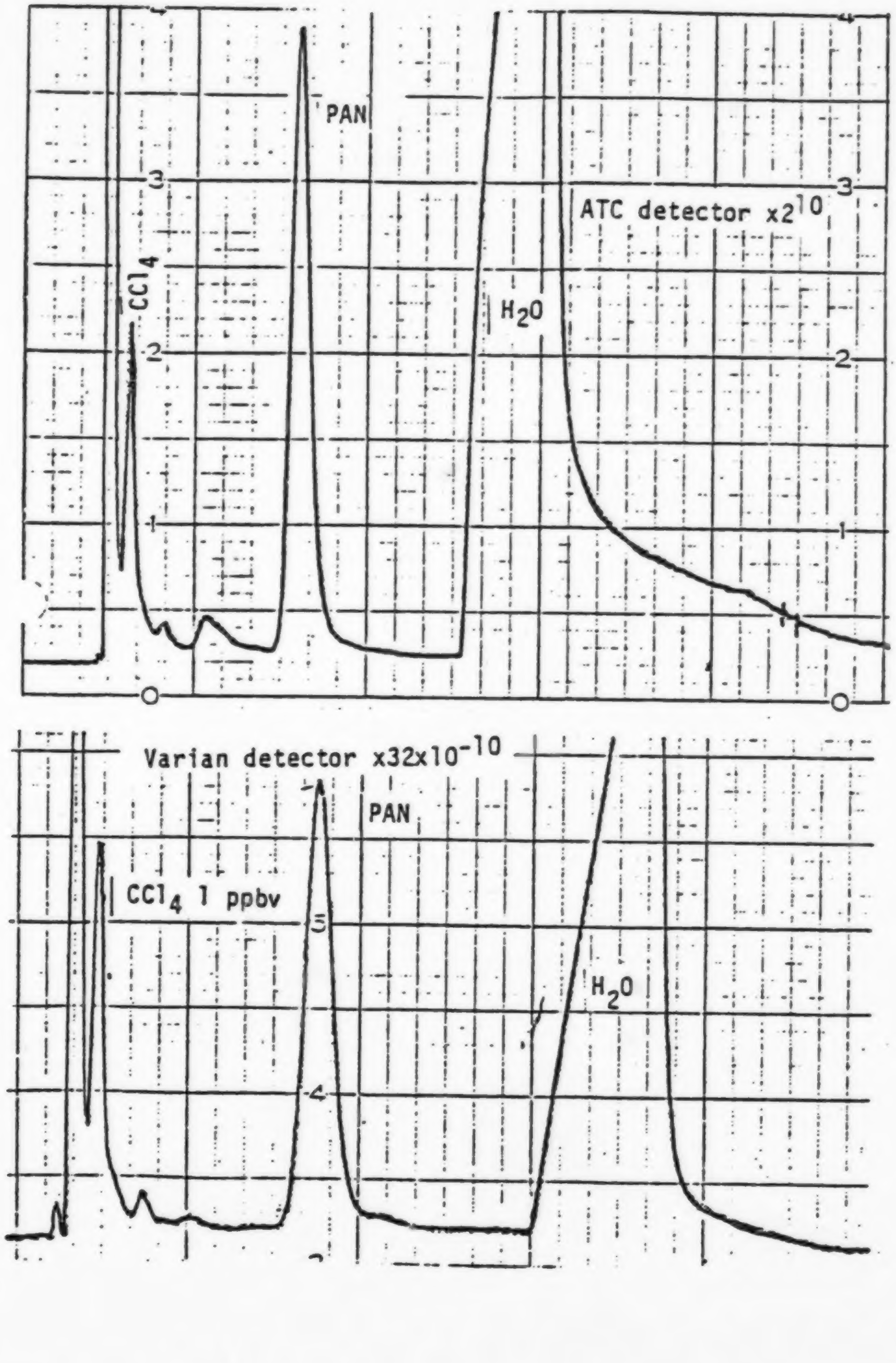


Figure 19. Response of two UNC electron capture detectors to 0.12 ppmV PAN May 1978.

Alkynitrates

The C_1–C_5 alkylnitrates can be detected on the same system that is used to measure PAN. Calibration for ethyl, isopropyl, propyl, and butylnitrates were performed by injecting microliter volumes of the authentic samples into the outdoor chambers and applying the appropriate dilution and temperature factors (Figure 20). Calibration factors for compounds for which we did not have authentic samples (*e.g.*, sec-butylnitrate and isopentylnitrate) were estimated from the ECD response of n-butylnitrate. An uncertainty of ±40% is assigned to these compounds with no authentic standards.

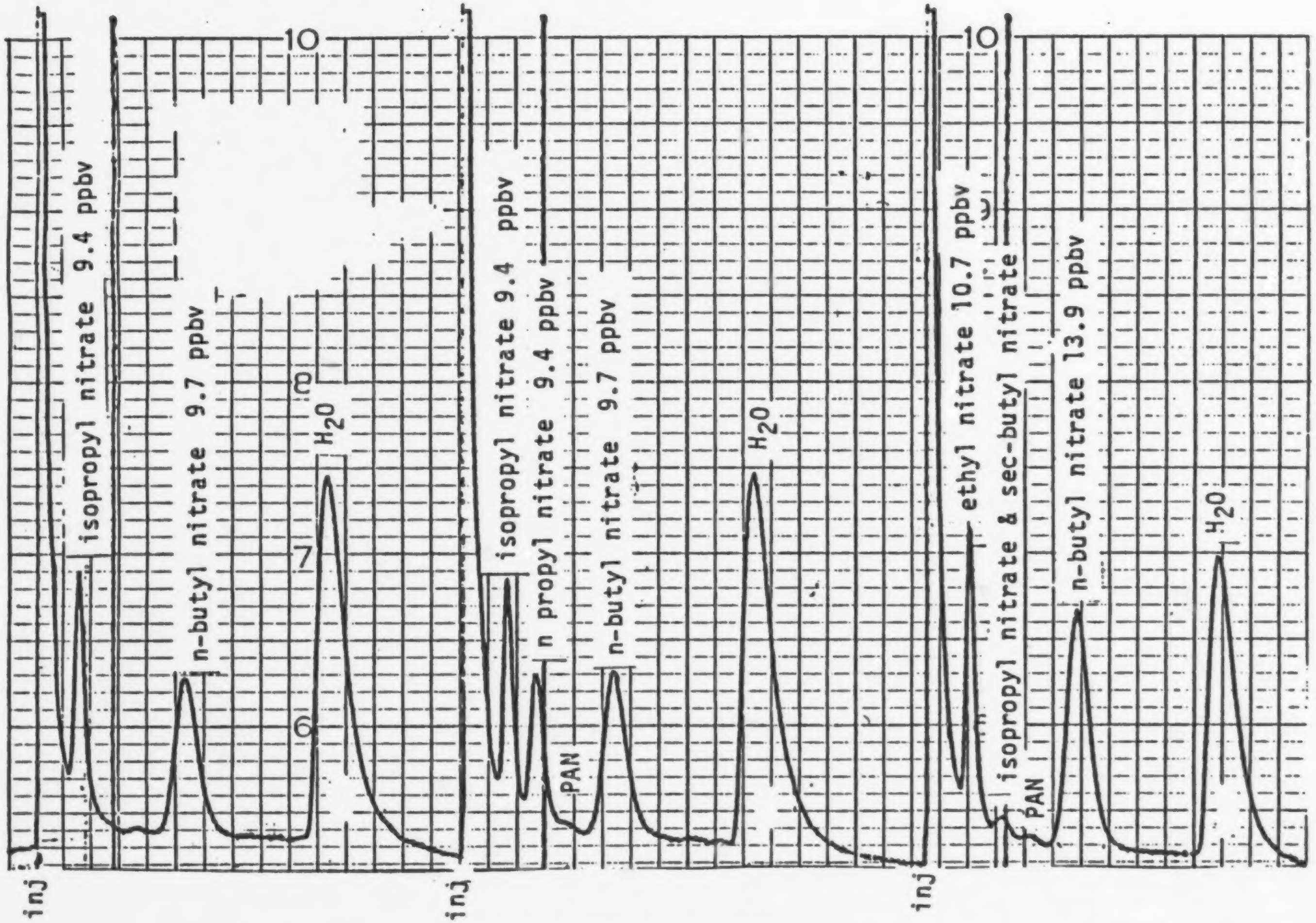


Figure 20. Detection of alkylnitrates with automated PAN GC, Varian 940 ECD. N_2 flow = 5 cc/min, oven and detector at 24.5°C, standing current on 32×10^{-9} amps = 91% of full scale, chart = .1"/min, atten. = $\times 32 \times 10^{-10}$ amps.

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Selected Data Tables

The purpose of this appendix is to present numerical data used to created many of the plots in the body of the report. Modelers may wish to have the exact numerical values to make calculations.

Table 1 list the HC class composition from dynamometer tests and gasoline analyses.

Table 2 lists the average carbon number in each HC class for each dynamometer test.

Table 3 lists the HC class composition for initial concentrations in selected chamber experiments.

Tables 4–9 list the individual HC species concentrations in the various HC compositional analyses performed.

Table 10 was added in the revision of this report based on data received after the report was finished. It lists the changes in HC species identifications made by MSERB in comparison to the original values supplied to UNC as part of the 1982–84 MSERB data supplied. For clarity, the changes that UNC made in the original MSERB species identifications are also listed.

Table 1. HC Class Composition for All Exhaust Samples from Dynamometer Tests and Gasoline Analyses.

Plym Vol, Amo Gas 1982

Class	FTP1	NYC1	Idle	GAS
Par	21.79	21.31	20.31	33.22
Ole	17.16	19.51	21.56	8.08
Aro	51.38	50.00	40.26	47.31
Acet	4.22	3.41	5.35	1.68
Unk	5.44	5.77	12.52	9.70
	99.99	100.00	100.00	99.99

Plym Vol, Ph66 Gas, 1983

Class	FTP	NYC1	Idle	GAS
Par	29.22	18.67	12.96	42.50
Ole	15.04	18.92	25.96	10.58
Aro	39.03	46.28	44.14	33.26
Acet	6.47	5.80	8.47	0.98
Unk	10.24	10.33	8.46	12.68
	100.00	100.00	99.99	100.00

Plym Vol, Ph66 Gas, 1984

Class	FTP	Hi Id	GAS
Par	30.11	48.18	42.50
Ole	20.24	11.35	10.58
Aro	30.68	24.48	33.26
Acet	15.35	11.08	0.98
Unk	3.61	4.90	12.68
	99.99	99.99	100.00

Plym Vol, Ph66 Gas, 1984 UNC Sam MSB anal

Class	UNC	MSB		GAS
Par	48.18	43.40		42.50
Ole	11.35	12.62		10.58
Aro	24.48	27.68		33.26
Acet	11.08	8.93		0.98
Unk	4.90	7.38		12.68
	99.99	100.01	0.00	100.00

Dodge Charger, Union 76 Gas 1982

Class	FTP1	NYC1	Idle	GAS
Par	25.00	24.00	18.00	41.37
Ole	19.00	24.00	29.00	11.68
Aro	34.00	37.00	35.00	37.07
Acet	13.00	10.00	10.00	1.62
Unk	7.00	3.00	7.00	8.26
	98.00	98.00	99.00	100.00

Dodge Charger, Ph66 Gas, 1983

Class	FTP	NYC1	Hi Id	GAS
Par	0.00	0.00	0.00	42.50
Ole	0.00	0.00	0.00	10.58
Aro	0.00	0.00	0.00	33.26
Acet	0.00	0.00	0.00	0.98
Unk	0.00	0.00	0.00	12.68
	0.00	0.00	0.00	100.00

Dodge Charger, Ph66 Gas, 1984

Class	FTP	Hi Id	GAS
Par	26.62	36.18	42.50
Ole	19.83	14.84	10.58
Aro	37.52	37.78	33.26
Acet	13.62	5.61	0.98
Unk	2.40	5.57	12.68
	99.99	99.98	100.00

Dodge Charger, Ph66 Gas, 1984 UNC Sam, MSB anal

Class	UNC	MSB		GAS
Par	36.18	31.88		42.50
Ole	14.84	23.90		10.58
Aro	37.78	26.19		33.26
Acet	5.61	9.38		0.98
Unk	5.57	8.65		12.68
	99.98	100.00	0.00	100.00

Table 2. Average Carbon Number in Each HC Class for All Exhaust Samples from Dynamometer Tests.

			PAR	OLE	ARO
1982	DC	FTP	5.19	2.67	8.17
		NYC	5.18	2.63	8.23
		HiId	4.35	2.55	7.89
	PV	FTP	5.1	2.6	7.9
		NYC	4.4	2.6	7.8
		HiId	4.6	2.7	7.7
1983	DC	FTP	0	0	0
		NYC	0	0	0
		HiId	0	0	0
	PV	FTP	5.9	3.2	8.1
		NYC	5.5	2.8	8.2
		HiId	4.7	2.6	7.9
1984	DC	FTP	5.3	2.5	7.8
			0	0	0
		HiId	5.5	2.8	7.8
	PV	FTP	5.3	2.4	7.9
			0	0	0
		HiId	5.8	3	7.8
MSB	VOC	FTP	5	2.9	8.3
		NYC	0	0	0

Table 3. HC Class Composition for the Initial Condition Injection for Selected Chamber Experiments.

Plym Vol, Union 76 NL Reg

Class	JN25	JN25	JN29	JN29	JN30	JN30	GAS	GAS
Par	7.64	6.55	17.44	17.45	9.91	9.40	45.91	41.37
eth+pro	29.82	28.73	18.16	18.30	22.67	20.92	12.96	11.68
Aro	59.27	62.18	51.95	51.06	60.01	58.00	41.13	37.07
Acet	10.55	10.36	12.93	12.62	13.72	12.16	0.00	0.00
	107.28	107.82	100.48	99.43	106.31	100.48	100.00	90.12

Dodge Charger, Phillips 66 NL Reg

Class	JL01	JL01	AU03	AU03	ST17	ST17	GAS	GAS
Par	13.86	13.78	19.66	21.71	25.84	25.00	49.22	42.50
eth+pro	24.59	23.23	23.18	21.09	16.87	16.71	12.25	10.58
Aro	42.29	38.91	40.05	35.74	32.82	36.57	38.52	33.26
Acet	20.06	20.40	16.47	12.65	22.16	21.71	0.00	0.00
	100.80	96.32	99.36	91.19	97.69	99.99	100.00	86.34

Plym Volare, Dodge Charger, Phillips 66 NL Reg

Class	JL02	JL02	JL15	JL15	AU11	AU11	OC04	GAS
Par	25.39	26.16	23.53	23.28	14.03	14.78	29.53	49.22
eth+pro	23.02	21.49	22.81	15.97	24.93	27.34	16.18	12.25
Aro	43.06	41.53	47.49	46.49	49.98	47.79	46.23	38.52
Acet	8.53	7.78	6.09	1.98	11.06	10.09	8.08	0.00
	100.00	96.96	99.92	87.72	100.00	100.00	100.02	100.00

Table 4. Individual HC Species Reported in 1982 Analysis of Plymouth Volare FTP,day1, FTP,day2, New York City Cycle, and Hot High Idle. MSB analysis, UNC identifications, normalized values.

1	METHANE	-164.0	0.0635	0.0691	0.0626	0.0737	1.0	M
2	ETHYLENE	-103.7	0.0849	0.0838	0.0937	0.0924	2.0	O
3	ETHANE	-88.6	0.0081	0.0102	0.0146	0.0115	2.0	P
4	ACETYLENE	-84.0	0.0324	0.0440	0.0250	0.0387	2.0	Y
5	PROPYLENE	-47.4	0.0279	0.0303	0.0353	0.0394	3.0	O
6	PROPANE	-42.1	0.0279	0.0303	0.0353	0.0394	3.0	P
7	PROPADIENE	-34.5	0.0018	0.0022	0.0026	0.0069	3.0	D
8	METHYL ACETYLENE	-23.2	0.0020	0.0026	0.0027	0.0088	3.0	Y
9	ISOBUTANE	-11.7	0.0018	0.0015	0.0016	0.0063	4.0	P
10	1-BUTENE	-6.3	0.0147	0.0156	0.0166	0.0155	4.0	O
12	N-BUTANE	-0.5	0.0154	0.0136	0.0401	0.0127	4.0	P
14	TRANS-2-BUTENE	0.9	0.0022	0.0022	0.0025	0.0045	4.0	O
15	CIS-2-BUTENE	3.7	0.0027	0.0033	0.0037	0.0078	4.0	O
16	3-METHYL-1-BUTENE	20.0	0.0006	0.0006	0.0006	0.0042	5.0	O
17	ISOPENTANE	27.8	0.0261	0.0249	0.0211	0.0125	5.0	P
18	1-PENTENE	30.0	0.0010	0.0010	0.0010	0.0000	5.0	O
19	N-PENTANE	36.0	0.0090	0.0066	0.0067	0.0051	5.0	P
21	TRANS-2-PENTENE	36.3	0.0027	0.0027	0.0024	0.0028	5.0	O
22	CIS-2-PENTENE	36.9	0.0014	0.0013	0.0012	0.0033	5.0	O
24	CYCLOPENTENE	44.0	0.0008	0.0007	0.0007	0.0045	5.0	C
25	CYCLOPENTANE	49.0	0.0013	0.0012	0.0012	0.0035	5.0	E
27	2,3-DIMETHYLBUTANE	58.0	0.0032	0.0030	0.0026	0.0022	6.0	P
28	2-METHYLPENTANE	62.0	0.0091	0.0087	0.0073	0.0050	6.0	P
29	2,3-DIMETHYL-1-BUTENE	55.7	0.0091	0.0087	0.0073	0.0050	6.0	O
30	3-METHYLPENTANE	63.6	0.0050	0.0042	0.0024	0.0060	6.0	P
31	1-HEXENE	63.0	0.0017	0.0018	0.0015	0.0035	6.0	O
33	N-HEXANE	69.0	0.0037	0.0025	0.0023	0.0047	6.0	P
35	2-METHYL-2-PENTENE	67.3	0.0022	0.0014	0.0015	0.0026	6.0	O
36	METHYLCYCLOPENTANE	71.8	0.0042	0.0038	0.0032	0.0063	6.0	E
38	2,4-DIMETHYLPENTANE	80.5	0.0031	0.0026	0.0027	0.0056	7.0	P
39	METHYLCYCLOPENTENE	75.0	0.0002	0.0001	0.0003	0.0000	6.0	C
40	BENZENE	80.0	0.0437	0.0501	0.0471	0.0578	6.0	A
42	2,3-DIMETHYLPENTANE	89.8	0.0075	0.0057	0.0052	0.0040	7.0	P
44	3-METHYLHEXANE	92.0	0.0021	0.0000	0.0000	0.0039	7.0	P
47	N-HEPTANE	98.4	0.0024	0.0020	0.0018	0.0030	7.0	P
49	METHYLCYCLOHEXANE	100.9	0.0009	0.0008	0.0007	0.0000	7.0	E
50	1-CIS-4-DIMETHYLCYCLOHEXANE	119.3	0.0008	0.0007	0.0005	0.0000	8.0	E
51	2,4-DIMETHYLHEXANE	110.0	0.0052	0.0044	0.0033	0.0062	8.0	P
53	2,3,4-TRIMETHYLPENTANE	113.4	0.0118	0.0049	0.0067	0.0000	8.0	P
54	2,3,3-TRIMETHYLPENTANE	115.0	0.0000	0.0050	0.0000	0.0000	8.0	P
55	TOLUENE	111.0	0.1753	0.1905	0.1630	0.1215	7.0	A
57	2-METHYLHEPTANE	117.6	0.0030	0.0026	0.0019	0.0000	8.0	P
58	3-METHYLHEPTANE	117.0	0.0021	0.0015	0.0012	0.0020	8.0	P
59	2,2,5-TRIMETHYLHEXANE	124.0	0.0068	0.0059	0.0040	0.0065	9.0	P
60	N-OCTANE	125.0	0.0021	0.0015	0.0011	0.0040	8.0	P
61	2,3,5-TRIMETHYLHEXANE	131.3	0.0015	0.0012	0.0008	0.0032	9.0	P
62	2,4-DIMETHYLHEPTANE	133.5	0.0009	0.0007	0.0007	0.0047	9.0	P
63	2,5-DIMETHYLHEPTANE	136.0	0.0012	0.0009	0.0007	0.0022	9.0	P
65	ETHYLBENZENE	136.2	0.0135	0.0134	0.0132	0.0120	8.0	A
66	2,3-DIMETHYLHEPTANE	140.5	0.0135	0.0134	0.0132	0.0120	9.0	P
67	P-XYLENE	138.3	0.0362	0.0346	0.0373	0.0262	8.0	A
68	M-XYLENE	139.1	0.0362	0.0346	0.0373	0.0262	8.0	A
69	4-METHYLOCTANE	141.0	0.0006	0.0006	0.0006	0.0036	9.0	P
70	3-METHYLOCTANE	143.0	0.0018	0.0013	0.0012	0.0000	9.0	P
71	O-XYLENE	144.0	0.0158	0.0145	0.0151	0.0137	9.0	A
72	NONANE	150.8	0.0017	0.0014	0.0015	0.0035	9.0	P
73	N-PROPYLBENZENE	159.0	0.0047	0.0038	0.0021	0.0033	9.0	A
78	1,2,4-TRIMETHYLBENZENE	169.3	0.0429	0.0415	0.0454	0.0290	9.0	A
79	SEC-BUTYLBENZENE	173.0	0.0026	0.0023	0.0028	0.0033	10.0	A
81	UNKNOWNS	-122.5	0.0510	0.0469	0.0541	0.1160	1.0	U
82	2,2,4-TRIMETHYLPENTANE	98.0	0.0128	0.0105	0.0080	0.0027	8.0	P
83	2-METHYL-2-BUTENE	39.0	0.0015	0.0015	0.0047	0.0032	5.0	O
92	UNDECANE	195.0	0.0026	0.0019	0.0026	0.0029	11.0	P
96	CIS-2-HEXENE	68.8	0.0000	0.0021	0.0000	0.0020	6.0	O
99	1,2,3-TRIMETHYLBENZENE	176.1	0.0088	0.0077	0.0072	0.0076	9.0	A
100	BUTYLBENZENE	183.0	0.0051	0.0043	0.0050	0.0015	10.0	A
118	1,3-DIETHYLBENZENE	181.0	0.0047	0.0042	0.0042	0.0002	10.0	A
120	1,2-DIETHYLBENZENE	183.4	0.0062	0.0059	0.0054	0.0079	10.0	A
84	M-ETHYLTOLUENE	161.0	0.0315	0.0298	0.0301	0.0153	10.0	A
157	4-METHYLHEPTANE	117.7	0.0038	0.0028	0.0023	0.0028	8.0	P
175	2-METHYL-1,3-BUTADIENE	34.0	0.0012	0.0018	0.0031	0.0000	5.0	D
176	2-METHYLOCTANE	142.8	0.0010	0.0007	0.0007	0.0000	9.0	P
177	TRANS-2-NONENE	0.0	0.0012	0.0008	0.0009	0.0000	9.0	O
154	1,3,5-TRIMETHYLBENZENE	164.7	0.0133	0.0126	0.0131	0.0086	9.0	A
86	O-ETHYLTOLUENE	162.0	0.0099	0.0087	0.0103	0.0072	10.0	A
180	CIS-PROPYLBENZENE	159.2	0.0014	0.0012	0.0015	0.0000	9.0	A
181	INDANE	176.5	0.0041	0.0039	0.0051	0.0041	9.0	A
182	4-PHENYL-1-BUTENE	177.0	0.0013	0.0006	0.0001	0.0082	10.0	A
183	1-METHYL-3N-PROPYLBENZENE	0.0	0.0034	0.0030	0.0026	0.0028	10.0	A
208	1-METHYLNAPHTHALENE	212.0	0.0095	0.0081	0.0101	0.0057	11.0	A
153	NAPHTHALENE	211.0	0.0075	0.0064	0.0070	0.0059	10.0	A
186	1-UNDECENE	192.7	0.0027	0.0025	0.0033	0.0021	11.0	O
187	TRANS-1-PHENYLBUTENE-1	198.7	0.0037	0.0031	0.0037	0.0047	10.0	A
188	HEXYNE	71.3	0.0007	0.0007	0.0005	0.0000	6.0	Y
189	PENTYNE	40.2	0.0043	0.0041	0.0037	0.0021	5.0	Y

Table 5. Individual HC Species Reported in 1983 Analysis of Plymouth Volare FTP, New York City Cycle, and Hot High Idle. MSB analysis, UNC identifications, normalized values.

1	METHANE	-164.0	0.0504	0.0823	0.0961	1.0	M
2	ETHYLENE	-103.7	0.0490	0.0808	0.1218	2.0	O
3	ETHANE	-88.6	0.0055	0.0064	0.0106	2.0	P
4	ACETYLENE	-84.0	0.0515	0.0464	0.0669	2.0	Y
5	PROPYLENE	-47.4	0.0184	0.0243	0.0419	3.0	O
6	PROPANE	-42.1	0.0032	0.0043	0.0074	3.0	P
7	PROPADIENE	-34.5	0.0000	0.0020	0.0046	3.0	D
8	METHYL ACETYLENE	-23.2	0.0045	0.0028	0.0074	3.0	Y
9	ISOBUTANE	-11.7	0.0059	0.0039	0.0030	4.0	P
10	1-BUTENE	-6.3	0.0105	0.0121	0.0181	4.0	O
12	N-BUTANE	-0.5	0.0189	0.0165	0.0181	4.0	P
13	1,3-BUTADIENE	-4.4	0.0047	0.0031	0.0045	4.0	D
14	TRANS-2-BUTENE	0.9	0.0037	0.0031	0.0031	4.0	O
15	CIS-2-BUTENE	3.7	0.0031	0.0039	0.0054	4.0	O
16	3-METHYL-1-BUTENE	20.0	0.0006	0.0005	0.0005	5.0	O
17	ISOPENTANE	27.8	0.0355	0.0198	0.0114	5.0	P
18	1-PENTENE	30.0	0.0022	0.0012	0.0011	5.0	O
19	N-PENTANE	36.0	0.0161	0.0103	0.0068	5.0	P
20	2-METHYL-1-BUTENE	31.2	0.0018	0.0011	0.0008	5.0	O
175	2-METHYL-1,3-BUTADIENE	34.0	0.0015	0.0024	0.0039	5.0	D
21	TRANS-2-PENTENE	36.3	0.0034	0.0024	0.0016	5.0	O
22	CIS-2-PENTENE	36.9	0.0018	0.0012	0.0008	5.0	O
189	PENTYNE	40.2	0.0045	0.0035	0.0022	5.0	Y
83	2-METHYL-2-BUTENE	39.0	0.0017	0.0051	0.0095	5.0	O
24	CYCLOPENTENE	44.0	0.0015	0.0010	0.0015	5.0	C
25	CYCLOPENTANE	49.0	0.0029	0.0014	0.0012	5.0	E
27	2,3-DIMETHYLBUTANE	58.0	0.0053	0.0026	0.0016	6.0	P
28	2-METHYLPENTANE	62.0	0.0216	0.0109	0.0065	6.0	P
30	3-METHYLPENTANE	63.6	0.0137	0.0072	0.0043	6.0	P
31	1-HEXENE	63.0	0.0021	0.0014	0.0012	6.0	O
33	N-HEXANE	69.0	0.0132	0.0083	0.0054	6.0	P
35	2-METHYL-2-PENTENE	67.3	0.0017	0.0003	0.0006	6.0	O
96	CIS-2-HEXENE	68.8	0.0027	0.0017	0.0000	6.0	O
188	HEXYNE	71.3	0.0009	0.0005	0.0001	6.0	Y
36	METHYLCYCLOPENTANE	71.8	0.0103	0.0054	0.0031	6.0	E
38	2,4-DIMETHYLPENTANE	80.5	0.0054	0.0028	0.0021	7.0	P
39	METHYLCYCLOPENTENE	75.0	0.0002	0.0003	0.0006	6.0	C
40	BENZENE	80.0	0.0316	0.0376	0.0575	6.0	A
41	CYCLOHEXENE	83.0	0.0215	0.0113	0.0044	6.0	C
44	3-METHYLHEXANE	92.0	0.0140	0.0083	0.0040	7.0	P
82	2,2,4-TRIMETHYLPENTANE	98.0	0.0152	0.0093	0.0046	8.0	P
47	N-HEPTANE	98.4	0.0106	0.0068	0.0041	7.0	P
48	2,4,4-TRIMETHYL-1-PENTENE	101.4	0.0045	0.0101	0.0051	8.0	O
49	METHYLCYCLOHEXANE	100.9	0.0015	0.0008	0.0013	7.0	E
50	1-CIS-4-DIMETHYLCYCLOHEXANE	119.3	0.0006	0.0004	0.0000	8.0	E
51	2,4-DIMETHYLHEXANE	110.0	0.0065	0.0042	0.0031	8.0	P
53	2,3,4-TRIMETHYLPENTANE	113.4	0.0060	0.0031	0.0000	8.0	P
54	2,3,3-TRIMETHYLPENTANE	115.0	0.0052	0.0042	0.0018	8.0	P
55	TOLUENE	111.0	0.0902	0.0881	0.0924	7.0	A
57	2-METHYLHEPTANE	117.6	0.0042	0.0056	0.0000	8.0	P
157	4-METHYLHEPTANE	117.7	0.0106	0.0045	0.0019	8.0	P
58	3-METHYLHEPTANE	117.0	0.0078	0.0027	0.0014	8.0	P
59	2,2,5-TRIMETHYLHEXANE	124.0	0.0032	0.0046	0.0008	9.0	P
60	N-OCTANE	125.0	0.0058	0.0009	0.0014	8.0	P
61	2,3,5-TRIMETHYLHEXANE	131.3	0.0016	0.0009	0.0003	9.0	P
62	2,4-DIMETHYLHEPTANE	133.5	0.0011	0.0009	0.0003	9.0	P
63	2,5-DIMETHYLHEPTANE	136.0	0.0027	0.0018	0.0007	9.0	P
65	ETHYLBENZENE	136.2	0.0166	0.0150	0.0124	8.0	A
68	M-XYLENE	139.1	0.0554	0.0615	0.0536	8.0	A
69	4-METHYLOCTANE	141.0	0.0057	0.0015	0.0003	9.0	P
70	3-METHYLOCTANE	143.0	0.0068	0.0026	0.0018	9.0	P
71	O-XYLENE	144.0	0.0218	0.0307	0.0301	9.0	A
176	2-METHYLOCTANE	142.8	0.0019	0.0008	0.0011	9.0	P
177	TRANS-2-NONENE	0.0	0.0030	0.0022	0.0008	9.0	O
72	NONANE	150.8	0.0028	0.0023	0.0014	9.0	P
73	N-PROPYLBENZENE	159.0	0.0073	0.0058	0.0031	9.0	A
84	M-ETHYLTOLUENE	161.0	0.0293	0.0335	0.0256	10.0	A
154	1,3,5-TRIMETHYLBENZENE	164.7	0.0118	0.0144	0.0111	9.0	A
86	O-ETHYLTOLUENE	162.0	0.0137	0.0124	0.0078	10.0	A
180	CIS-PROPYLBENZENE	159.2	0.0026	0.0003	0.0002	9.0	A
78	1,2,4-TRIMETHYLBENZENE	169.3	0.0359	0.0477	0.0416	9.0	A
79	SEC-BUTYLBENZENE	173.0	0.0018	0.0009	0.0000	10.0	A
80	N-DECANE	174.0	0.0019	0.0015	0.0010	10.0	P
99	1,2,3-TRIMETHYLBENZENE	176.1	0.0069	0.0105	0.0078	9.0	A
181	INDANE	176.5	0.0046	0.0054	0.0043	9.0	A
182	4-PHENYL-1-BUTENE	177.0	0.0039	0.0063	0.0107	10.0	A
183	1-METHYL-3N-PROPYLBENZENE	0.0	0.0032	0.0039	0.0028	10.0	A
118	1,3-DIETHYLBENZENE	181.0	0.0052	0.0058	0.0033	10.0	A
100	BUTYLBENZENE	183.0	0.0049	0.0053	0.0033	10.0	A
120	1,2-DIETHYLBENZENE	183.4	0.0065	0.0080	0.0059	10.0	A
208	1-METHYLNAPHTHALENE	212.0	0.0056	0.0129	0.0083	11.0	A
153	NAPHTHALENE	211.0	0.0072	0.0107	0.0096	10.0	A
186	1-UNDECENE	192.7	0.0033	0.0020	0.0031	11.0	O
92	UNDECANE	195.0	0.0042	0.0039	0.0043	11.0	P
87	TERT-BUTYLBENZENE	169.0	0.0047	0.0081	0.0076	10.0	A
81	UNKNOWNS	-122.5	0.0973	0.0948	0.0765	1.0	U

Table 6. Individual HC Species Reported in 1984 Analysis of Dodge Charger, FTP, High Idle, Plymouth Volare, FTP, High Idle. MSB analysis, UNC identifications, normalized values.

2	ETHYLENE	-103.7	0.1066	0.0615	0.1207	0.0444	2.0	O
3	ETHANE	-88.6	0.0080	0.0074	0.0136	0.0041	2.0	P
4	ACETYLENE	-84.0	0.1341	0.0510	0.1511	0.1028	2.0	Y
5	PROPYLENE	-47.4	0.0428	0.0280	0.0394	0.0117	3.0	O
6	PROPANE	-42.1	0.0116	0.0026	0.0119	0.0044	3.0	P
9	ISOBUTANE	-11.7	0.0058	0.0103	0.0036	0.0073	4.0	P
10	1-BUTENE	-6.3	0.0099	0.0086	0.0077	0.0041	4.0	O
13	1,3-BUTADIENE	-4.4	0.0105	0.0057	0.0087	0.0030	4.0	D
12	N-BUTANE	-0.5	0.0337	0.0417	0.0435	0.0632	4.0	P
14	TRANS-2-BUTENE	0.9	0.0038	0.0062	0.0032	0.0034	4.0	O
15	CIS-2-BUTENE	3.7	0.0034	0.0048	0.0028	0.0028	4.0	O
81	UNKNOWNS	-122.5	0.0019	0.0028	0.0014	0.0028	1.0	U
16	3-METHYL-1-BUTENE	20.0	0.0021	0.0030	0.0019	0.0026	5.0	O
17	ISOPENTANE	27.8	0.0344	0.0552	0.0362	0.0720	5.0	P
18	1-PENTENE	30.0	0.0019	0.0027	0.0017	0.0025	5.0	O
20	2-METHYL-1-BUTENE	31.2	0.0030	0.0044	0.0028	0.0032	5.0	O
19	N-PENTANE	36.0	0.0163	0.0263	0.0136	0.0279	5.0	P
175	2-METHYL-1,3-BUTADIENE	34.0	0.0029	0.0051	0.0031	0.0064	5.0	D
21	TRANS-2-PENTENE	36.3	0.0016	0.0028	0.0017	0.0033	5.0	O
22	CIS-2-PENTENE	36.9	0.0021	0.0051	0.0024	0.0080	5.0	O
189	PENTYNE	40.2	0.0021	0.0051	0.0024	0.0080	5.0	Y
83	2-METHYL-2-BUTENE	39.0	0.0020	0.0028	0.0010	0.0019	5.0	O
24	CYCLOPENTENE	44.0	0.0010	0.0015	0.0009	0.0016	5.0	C
25	CYCLOPENTANE	49.0	0.0018	0.0029	0.0015	0.0037	5.0	E
23	2,2-DIMETHYLBUTANE	50.0	0.0041	0.0069	0.0057	0.0114	6.0	P
28	2-METHYLPENTANE	62.0	0.0180	0.0285	0.0142	0.0278	6.0	P
30	3-METHYLPENTANE	63.6	0.0117	0.0189	0.0082	0.0153	6.0	P
31	1-HEXENE	63.0	0.0017	0.0013	0.0009	0.0033	6.0	O
33	N-HEXANE	69.0	0.0117	0.0181	0.0057	0.0104	6.0	P
149	2-HEXENE	68.0	0.0017	0.0029	0.0023	0.0066	6.0	O
96	CIS-2-HEXENE	68.8	0.0011	0.0023	0.0013	0.0046	6.0	O
36	METHYLCYCLOPENTANE	71.8	0.0076	0.0131	0.0063	0.0133	6.0	E
38	2,4-DIMETHYLPENTANE	80.5	0.0033	0.0057	0.0045	0.0086	7.0	P
40	BENZENE	80.0	0.0546	0.0394	0.0417	0.0211	6.0	A
45	CYCLOHEXANE	81.0	0.0016	0.0026	0.0011	0.0016	6.0	E
42	2,3-DIMETHYLPENTANE	89.8	0.0163	0.0259	0.0124	0.0226	7.0	P
44	3-METHYLHEXANE	92.0	0.0104	0.0145	0.0066	0.0110	7.0	P
43	2-METHYLHEXANE	90.0	0.0023	0.0023	0.0016	0.0035	7.0	P
44	3-METHYLHEXANE	92.0	0.0019	0.0018	0.0013	0.0026	7.0	P
82	2,2,4-TRIMETHYLPENTANE	98.0	0.0112	0.0146	0.0321	0.0559	8.0	P
47	N-HEPTANE	98.4	0.0091	0.0112	0.0057	0.0095	7.0	P
49	METHYLCYCLOHEXANE	100.9	0.0035	0.0039	0.0042	0.0064	7.0	E
52	2,5-DIMETHYLHEXANE	109.0	0.0027	0.0031	0.0071	0.0113	8.0	P
114	2,2,3-TRIMETHYLPENTANE	110.0	0.0027	0.0030	0.0048	0.0068	8.0	P
51	2,4-DIMETHYLHEXANE	110.0	0.0048	0.0051	0.0124	0.0231	8.0	P
55	TOLUENE	111.0	0.1090	0.1239	0.0769	0.0821	7.0	A
53	2,3,4-TRIMETHYLPENTANE	113.4	0.0025	0.0034	0.0045	0.0078	8.0	P
157	4-METHYLHEPTANE	117.7	0.0063	0.0086	0.0062	0.0100	8.0	P
54	2,3,3-TRIMETHYLPENTANE	115.0	0.0063	0.0083	0.0059	0.0091	8.0	P
59	2,2,5-TRIMETHYLHEXANE	124.0	0.0032	0.0022	0.0097	0.0129	9.0	P
60	N-OCTANE	125.0	0.0045	0.0052	0.0045	0.0061	8.0	P
61	2,3,5-TRIMETHYLHEXANE	131.3	0.0015	0.0008	0.0022	0.0015	9.0	P
62	2,4-DIMETHYLHEPTANE	133.5	0.0018	0.0019	0.0025	0.0030	9.0	P
65	ETHYLBENZENE	136.2	0.0166	0.0180	0.0134	0.0127	8.0	A
68	M-XYLENE	139.1	0.0569	0.0586	0.0490	0.0437	8.0	A
70	3-METHYLOCTANE	143.0	0.0032	0.0036	0.0038	0.0044	9.0	P
89	STYRENE	145.0	0.0056	0.0052	0.0051	0.0043	8.0	A
71	O-XYLENE	144.0	0.0207	0.0225	0.0179	0.0158	9.0	A
72	NONANE	150.8	0.0029	0.0021	0.0040	0.0034	9.0	P
88	ISOPROPYLBENZENE	152.4	0.0017	0.0013	0.0016	0.0008	9.0	A
81	UNKNOWNS	-122.5	0.0020	0.0021	0.0023	0.0012	1.0	U
73	N-PROPYLBENZENE	159.0	0.0047	0.0051	0.0036	0.0034	9.0	A
84	M-ETHYLTOLUENE	161.0	0.0172	0.0191	0.0142	0.0110	10.0	A
85	P-ETHYLTOLUENE	162.0	0.0062	0.0069	0.0051	0.0040	10.0	A
154	1,3,5-TRIMETHYLBENZENE	164.7	0.0081	0.0084	0.0068	0.0052	9.0	A
86	O-ETHYLTOLUENE	162.0	0.0083	0.0091	0.0082	0.0067	10.0	A
78	1,2,4-TRIMETHYLBENZENE	169.3	0.0265	0.0273	0.0219	0.0148	9.0	A
79	SEC-BUTYLBENZENE	173.0	0.0020	0.0015	0.0028	0.0017	10.0	A
99	1,2,3-TRIMETHYLBENZENE	176.1	0.0062	0.0063	0.0051	0.0032	9.0	A
181	INDANE	176.5	0.0027	0.0027	0.0035	0.0026	9.0	A
118	1,3-DIETHYLBENZENE	181.0	0.0057	0.0028	0.0057	0.0012	10.0	A
120	1,2-DIETHYLBENZENE	183.4	0.0056	0.0027	0.0048	0.0012	10.0	A
100	BUTYLBENZENE	183.0	0.0050	0.0052	0.0051	0.0033	10.0	A
119	1,4-DIETHYLBENZENE	183.8	0.0042	0.0048	0.0044	0.0028	10.0	A
174	TETRAMETHYLBENZENE	198.0	0.0033	0.0015	0.0039	0.0007	10.0	A
193		0.0	0.0014	0.0019	0.0028	0.0013	0.0	Z
153	NAPHTHALENE	211.0	0.0026	0.0029	0.0029	0.0012	10.0	A
208	1-METHYLNAPHTHALENE	212.0	0.0003	0.0005	0.0002	0.0001	11.0	A
209		0.0	0.0001	0.0002	0.0001	0.0000	0.0	Z
81	UNKNOWNS	-122.5	0.0201	0.0508	0.0324	0.0450	1.0	U

Table 7. Individual HC Species Reported in 1984 Analysis of Plymouth Volare Cold High Idle, Dodge Charger Cold High Idle. MSB anaylsis, UNC identifications, normalized values.

1	METHANE	-164.0	0.0419	0.0638	1.0	M
2	ETHYLENE	-103.7	0.0273	0.0982	2.0	O
3	ETHANE	-88.6	0.0027	0.0098	2.0	P
4	ACETYLENE	-84.0	0.0697	0.0724	2.0	Y
5	PROPYLENE	-47.4	0.0020	0.0399	3.0	O
6	PROPANE	-42.1	0.0002	0.0045	3.0	P
7	PROPADIENE	-34.5	0.0000	0.0000	3.0	D
8	METHYL ACETYLENE	-23.2	0.0000	0.0092	3.0	Y
9	ISOBUTANE	-11.7	0.0110	0.0064	4.0	P
10	1-BUTENE	-6.3	0.0000	0.0132	4.0	O
12	N-BUTANE	-0.5	0.0368	0.0370	4.0	P
13	1,3-BUTADIENE	-4.4	0.0092	0.0093	4.0	D
14	TRANS-2-BUTENE	0.9	0.0060	0.0042	4.0	O
15	CIS-2-BUTENE	3.7	0.0061	0.0054	4.0	O
16	3-METHYL-1-BUTENE	20.0	0.0009	0.0011	5.0	O
17	ISOPENTANE	27.8	0.0618	0.0459	5.0	P
18	1-PENTENE	30.0	0.0025	0.0024	5.0	O
19	N-PENTANE	36.0	0.0266	0.0267	5.0	P
20	2-METHYL-1-BUTENE	31.2	0.0030	0.0030	5.0	O
175	2-METHYL-1,3-BUTADIENE	34.0	0.0011	0.0028	5.0	D
21	TRANS-2-PENTENE	36.3	0.0068	0.0049	5.0	O
22	CIS-2-PENTENE	36.9	0.0034	0.0028	5.0	O
189	PENTYNE	40.2	0.0062	0.0053	5.0	Y
83	2-METHYL-2-BUTENE	39.0	0.0029	0.0007	5.0	O
24	CYCLOPENTENE	44.0	0.0014	0.0013	5.0	C
25	CYCLOPENTANE	49.0	0.0040	0.0037	5.0	E
27	2,3-DIMETHYLBUTANE	58.0	0.0079	0.0053	6.0	P
28	2-METHYLPENTANE	62.0	0.0320	0.0246	6.0	P
30	3-METHYLPENTANE	63.6	0.0209	0.0156	6.0	P
31	1-HEXENE	63.0	0.0030	0.0024	6.0	O
33	N-HEXANE	69.0	0.0197	0.0187	6.0	P
35	2-METHYL-2-PENTENE	67.3	0.0027	0.0020	6.0	O
96	CIS-2-HEXENE	68.8	0.0039	0.0025	6.0	O
188	HEXYNE	71.3	0.0014	0.0010	6.0	Y
36	METHYLCYCLOPENTANE	71.8	0.0117	0.0098	6.0	E
38	2,4-DIMETHYLPENTANE	80.5	0.0067	0.0038	7.0	P
39	METHYLCYCLOPENTENE	75.0	0.0001	0.0000	6.0	C
40	BENZENE	80.0	0.0255	0.0382	6.0	A
41	CYCLOHEXENE	83.0	0.0128	0.0175	6.0	C
44	3-METHYLHEXANE	92.0	0.0171	0.0134	7.0	P
82	2,2,4-TRIMETHYLPENTANE	98.0	0.0191	0.0079	8.0	P
47	N-HEPTANE	98.4	0.0199	0.0104	7.0	P
48	2,4,4-TRIMETHYL-1-PENTENE	101.4	0.0130	0.0063	8.0	O
49	METHYLCYCLOHEXANE	100.9	0.0062	0.0015	7.0	E
50	1-CIS-4-DIMETHYLCYCLOHEXANE	119.3	0.0019	0.0000	8.0	E
51	2,4-DIMETHYLHEXANE	110.0	0.0078	0.0044	8.0	P
53	2,3,4-TRIMETHYLPENTANE	113.4	0.0071	0.0023	8.0	P
54	2,3,3-TRIMETHYLPENTANE	115.0	0.0069	0.0027	8.0	P
55	TOLUENE	111.0	0.0936	0.0584	7.0	A
57	2-METHYLHEPTANE	117.6	0.0042	0.0025	8.0	P
157	4-METHYLHEPTANE	117.7	0.0071	0.0087	8.0	P
58	3-METHYLHEPTANE	117.0	0.0086	0.0058	8.0	P
59	2,2,5-TRIMETHYLHEXANE	124.0	0.0041	0.0025	9.0	P
60	N-OCTANE	125.0	0.0070	0.0055	8.0	P
61	2,3,5-TRIMETHYLHEXANE	131.3	0.0009	0.0013	9.0	P
62	2,4-DIMETHYLHEPTANE	133.5	0.0016	0.0004	9.0	P
63	2,5-DIMETHYLHEPTANE	136.0	0.0025	0.0020	9.0	P
65	ETHYLBENZENE	136.2	0.0137	0.0108	8.0	A
68	M-XYLENE	139.1	0.0422	0.0380	8.0	A
69	4-METHYLOCTANE	141.0	0.0047	0.0038	9.0	P
70	3-METHYLOCTANE	143.0	0.0035	0.0051	9.0	P
71	O-XYLENE	144.0	0.0154	0.0135	9.0	A
176	2-METHYLOCTANE	142.8	0.0009	0.0016	9.0	P
177	TRANS-2-NONENE	0.0	0.0007	0.0022	9.0	O
72	NONANE	150.8	0.0019	0.0015	9.0	P
73	N-PROPYLBENZENE	159.0	0.0034	0.0043	9.0	A
84	M-ETHYLTOLUENE	161.0	0.0132	0.0170	10.0	A
154	1,3,5-TRIMETHYLBENZENE	164.7	0.0043	0.0067	9.0	A
86	O-ETHYLTOLUENE	162.0	0.0051	0.0055	10.0	A
180	CIS-PROPYLBENZENE	159.2	0.0009	0.0015	9.0	A
78	1,2,4-TRIMETHYLBENZENE	169.3	0.0111	0.0194	9.0	A
79	SEC-BUTYLBENZENE	173.0	0.0006	0.0007	10.0	A
80	N-DECANE	174.0	0.0004	0.0007	10.0	P
99	1,2,3-TRIMETHYLBENZENE	176.1	0.0006	0.0015	9.0	A
181	INDANE	176.5	0.0022	0.0045	9.0	A
182	4-PHENYL-1-BUTENE	177.0	0.0011	0.0029	10.0	A
183	1-METHYL-3N-PROPYLBENZENE	0.0	0.0007	0.0017	10.0	A
118	1,3-DIETHYLBENZENE	181.0	0.0012	0.0029	10.0	A
100	BUTYLBENZENE	183.0	0.0011	0.0027	10.0	A
120	1,2-DIETHYLBENZENE	183.4	0.0012	0.0038	10.0	A
208	1-METHYLNAPHTHALENE	212.0	0.0009	0.0035	11.0	A
153	NAPHTHALENE	211.0	0.0011	0.0051	10.0	A
186	1-UNDECENE	192.7	0.0004	0.0018	11.0	O
92	UNDECANE	195.0	0.0005	0.0027	11.0	P
187	TRANS-1-PHENYLBUTENE-1	198.7	0.0005	0.0026	10.0	A
81	UNKNOWNS	-122.5	0.0639	0.0810	1.0	U

Table 8. Average of Individual HC Species Reported in MSB/46-car VOC Study. MSB analysis, UNC identifications, normalized values.

2	ETHYLENE	-103.7	0.0880	0.0847	2.0	O
3	ETHANE	-88.6	0.0250	0.0197	2.0	P
4	ACETYLENE	-84.0	0.0267	0.0196	2.0	Y
5	PROPYLENE	-47.4	0.0271	0.0216	3.0	O
6	PROPANE	-42.1	0.0030	0.0024	3.0	P
7	PROPADIENE	-34.5	0.0013	0.0010	3.0	D
8	METHYL ACETYLENE	-23.2	0.0013	0.0012	3.0	Y
9	ISOBUTANE	-11.7	0.0082	0.0079	4.0	P
10	1-BUTENE	-6.3	0.0149	0.0150	4.0	O
12	N-BUTANE	-0.5	0.0458	0.0438	4.0	P
13	1,3-BUTADIENE	-4.4	0.0115	0.0109	4.0	D
14	TRANS-2-BUTENE	0.9	0.0039	0.0044	4.0	O
15	CIS-2-BUTENE	3.7	0.0053	0.0047	4.0	O
16	3-METHYL-1-BUTENE	20.0	0.0023	0.0016	5.0	O
17	ISOPENTANE	27.8	0.0441	0.0433	5.0	P
18	1-PENTENE	30.0	0.0027	0.0021	5.0	O
19	N-PENTANE	36.0	0.0200	0.0193	5.0	P
21	TRANS-2-PENTENE	36.3	0.0039	0.0035	5.0	O
22	CIS-2-PENTENE	36.9	0.0024	0.0024	5.0	O
189	PENTYNE	40.2	0.0056	0.0063	5.0	Y
83	2-METHYL-2-BUTENE	39.0	0.0040	0.0042	5.0	O
24	CYCLOPENTENE	44.0	0.0022	0.0029	5.0	C
25	CYCLOPENTANE	49.0	0.0038	0.0026	5.0	E
27	2,3-DIMETHYLBUTANE	58.0	0.0072	0.0056	6.0	P
28	2-METHYLPENTANE	62.0	0.0173	0.0134	6.0	P
30	3-METHYLPENTANE	63.6	0.0124	0.0091	6.0	P
31	1-HEXENE	63.0	0.0024	0.0026	6.0	O
33	N-HEXANE	69.0	0.0084	0.0079	6.0	P
35	2-METHYL-2-PENTENE	67.3	0.0026	0.0025	6.0	O
96	CIS-2-HEXENE	68.8	0.0024	0.0034	6.0	O
188	HEXYNE	71.3	0.0008	0.0011	6.0	Y
36	METHYLCYCLOPENTANE	71.8	0.0084	0.0072	6.0	E
38	2,4-DIMETHYLPENTANE	80.5	0.0074	0.0064	7.0	P
39	METHYLCYCLOPENTENE	75.0	0.0003	0.0002	6.0	C
40	BENZENE	80.0	0.0381	0.0294	6.0	A
41	CYCLOHEXENE	83.0	0.0173	0.0145	6.0	C
44	3-METHYLHEXANE	92.0	0.0124	0.0103	7.0	P
82	2,2,4-TRIMETHYLPENTANE	98.0	0.0265	0.0224	8.0	P
47	N-HEPTANE	98.4	0.0070	0.0062	7.0	P
48	2,4,4-TRIMETHYL-1-PENTENE	101.4	0.0068	0.0025	8.0	O
49	METHYLCYCLOHEXANE	100.9	0.0015	0.0015	7.0	E
50	1-CIS-4-DIMETHYLCYCLOHEXANE	119.3	0.0008	0.0007	8.0	E
51	2,4-DIMETHYLHEXANE	110.0	0.0087	0.0070	8.0	P
53	2,3,4-TRIMETHYLPENTANE	113.4	0.0017	0.0014	8.0	P
54	2,3,3-TRIMETHYLPENTANE	115.0	0.0146	0.0129	8.0	P
55	TOLUENE	111.0	0.0662	0.0662	7.0	A
57	2-METHYLHEPTANE	117.6	0.0029	0.0024	8.0	P
58	3-METHYLHEPTANE	117.0	0.0049	0.0042	8.0	P
59	2,2,5-TRIMETHYLHEXANE	124.0	0.0067	0.0051	9.0	P
60	N-OCTANE	125.0	0.0040	0.0035	8.0	P
61	2,3,5-TRIMETHYLHEXANE	131.3	0.0014	0.0013	9.0	P
62	2,4-DIMETHYLHEPTANE	133.5	0.0015	0.0015	9.0	P
63	2,5-DIMETHYLHEPTANE	136.0	0.0025	0.0018	9.0	P
65	ETHYLBENZENE	136.2	0.0100	0.0107	8.0	A
67	P-XYLENE	138.3	0.0313	0.0351	8.0	A
69	4-METHYLOCTANE	141.0	0.0002	0.0002	9.0	P
70	3-METHYLOCTANE	143.0	0.0039	0.0030	9.0	P
71	O-XYLENE	144.0	0.0210	0.0214	9.0	A
176	2-METHYLOCTANE	142.8	0.0009	0.0010	9.0	P
177	TRANS-2-NONENE	0.0	0.0028	0.0024	9.0	O
72	NONANE	150.8	0.0024	0.0024	9.0	P
73	N-PROPYLBENZENE	159.0	0.0065	0.0081	9.0	A
84	M-ETHYLTOLUENE	161.0	0.0241	0.0286	10.0	A
154	1,3,5-TRIMETHYLBENZENE	164.7	0.0110	0.0125	9.0	A
86	O-ETHYLTOLUENE	162.0	0.0153	0.0166	10.0	A
180	CIS-PROPYLBENZENE	159.2	0.0027	0.0034	9.0	A
78	1,2,4-TRIMETHYLBENZENE	169.3	0.0314	0.0375	9.0	A
79	SEC-BUTYLBENZENE	173.0	0.0015	0.0020	10.0	A
80	N-DECANE	174.0	0.0018	0.0029	10.0	P
99	1,2,3-TRIMETHYLBENZENE	176.1	0.0086	0.0100	9.0	A
181	INDANE	176.5	0.0055	0.0072	9.0	A
182	4-PHENYL-1-BUTENE	177.0	0.0037	0.0043	10.0	A
183	1-METHYL-3N-PROPYLBENZENE	0.0	0.0035	0.0042	10.0	A
118	1,3-DIETHYLBENZENE	181.0	0.0067	0.0079	10.0	A
100	BUTYLBENZENE	183.0	0.0049	0.0068	10.0	A
120	1,2-DIETHYLBENZENE	183.4	0.0070	0.0093	10.0	A
208	1-METHYLNAPHTHALENE	212.0	0.0136	0.0181	11.0	A
153	NAPHTHALENE	211.0	0.0119	0.0172	10.0	A
186	1-UNDECENE	192.7	0.0067	0.0086	11.0	O
80	N-DECANE	174.0	0.0077	0.0080	10.0	P
187	TRANS-1-PHENYLBUTENE-1	198.7	0.0063	0.0103	10.0	A
81	UNKNOWNS	-122.5	0.0986	0.1212	1.0	U

Table 9. Individual HC Species Reported in Amoco Premium, Union 76 Non-Leaded Regular, and Phillips 66 Non-Leaded Regular Gasoline. MSB analysis, UNC identifications, normalized values.

1	METHANE	-164.0	0.0342	0.0509	0.0365	1.0	M
2	ETHYLENE	-103.7	0.0015	0.0034	0.0013	2.0	O
3	ETHANE	-88.6	0.0000	0.0000	0.0005	2.0	P
4	ACETYLENE	-84.0	0.0000	0.0000	0.0000	2.0	Y
5	PROPYLENE	-47.4	0.0056	0.0063	0.0065	3.0	O
6	PROPANE	-42.1	0.0006	0.0007	0.0007	3.0	P
7	PROPADIENE	-34.5	0.0000	0.0000	0.0000	3.0	D
8	METHYL ACETYLENE	-23.2	0.0000	0.0000	0.0000	3.0	Y
9	ISOBUTANE	-11.7	0.0134	0.0185	0.0190	4.0	P
10	1-BUTENE	-6.3	0.0000	0.0000	0.0000	4.0	O
12	N-BUTANE	-0.5	0.0270	0.0181	0.0630	4.0	P
13	1,3-BUTADIENE	-4.4	0.0067	0.0045	0.0157	4.0	D
14	TRANS-2-BUTENE	0.9	0.0012	0.0025	0.0014	4.0	O
15	CIS-2-BUTENE	3.7	0.0012	0.0025	0.0014	4.0	O
16	3-METHYL-1-BUTENE	20.0	0.0006	0.0009	0.0005	5.0	O
17	ISOPENTANE	27.8	0.0682	0.0612	0.0502	5.0	P
18	1-PENTENE	30.0	0.0017	0.0031	0.0013	5.0	O
19	N-PENTANE	36.0	0.0205	0.0273	0.0236	5.0	P
20	2-METHYL-1-BUTENE	31.2	0.0023	0.0030	0.0026	5.0	O
175	2-METHYL-1,3-BUTADIENE	34.0	0.0000	0.0000	0.0000	5.0	D
21	TRANS-2-PENTENE	36.3	0.0070	0.0089	0.0053	5.0	O
22	CIS-2-PENTENE	36.9	0.0040	0.0051	0.0031	5.0	O
189	PENTYNE	40.2	0.0143	0.0121	0.0075	5.0	Y
83	2-METHYL-2-BUTENE	39.0	0.0007	0.0040	0.0037	5.0	O
24	CYCLOPENTENE	44.0	0.0030	0.0036	0.0036	5.0	C
25	CYCLOPENTANE	49.0	0.0040	0.0049	0.0046	5.0	E
27	2,3-DIMETHYLBUTANE	58.0	0.0075	0.0085	0.0085	6.0	P
28	2-METHYLPENTANE	62.0	0.0265	0.0273	0.0218	6.0	P
30	3-METHYLPENTANE	63.6	0.0141	0.0176	0.0154	6.0	P
31	1-HEXENE	63.0	0.0061	0.0063	0.0050	6.0	O
33	N-HEXANE	69.0	0.0080	0.0130	0.0143	6.0	P
35	2-METHYL-2-PENTENE	67.3	0.0070	0.0080	0.0043	6.0	O
96	CIS-2-HEXENE	68.8	0.0062	0.0060	0.0043	6.0	O
188	HEXYNE	71.3	0.0026	0.0033	0.0019	6.0	Y
36	METHYLCYCLOPENTANE	71.8	0.0073	0.0116	0.0129	6.0	E
38	2,4-DIMETHYLPENTANE	80.5	0.0082	0.0114	0.0115	7.0	P
39	METHYLCYCLOPENTENE	75.0	0.0000	0.0000	0.0000	6.0	C
40	BENZENE	80.0	0.0188	0.0176	0.0523	6.0	A
41	CYCLOHEXENE	83.0	0.0126	0.0271	0.0243	6.0	C
44	3-METHYLHEXANE	92.0	0.0099	0.0190	0.0160	7.0	P
82	2,2,4-TRIMETHYLPENTANE	98.0	0.0199	0.0373	0.0298	8.0	P
47	N-HEPTANE	98.4	0.0041	0.0123	0.0114	7.0	P
48	2,4,4-TRIMETHYL-1-PENTENE	101.4	0.0016	0.0078	0.0066	8.0	O
44	3-METHYLHEXANE	92.0	0.0016	0.0078	0.0066	7.0	P
49	METHYLCYCLOHEXANE	100.9	0.0024	0.0029	0.0031	7.0	E
50	1-CIS-4-DIMETHYLCYCLOHEXANE	119.3	0.0017	0.0013	0.0015	8.0	E
51	2,4-DIMETHYLHEXANE	110.0	0.0081	0.0114	0.0106	8.0	P
53	2,3,4-TRIMETHYLPENTANE	113.4	0.0000	0.0000	0.0000	8.0	P
54	2,3,3-TRIMETHYLPENTANE	115.0	0.0174	0.0224	0.0169	8.0	P
55	TOLUENE	111.0	0.1941	0.0550	0.0312	7.0	A
57	2-METHYLHEPTANE	117.6	0.0010	0.0036	0.0061	8.0	P
157	4-METHYLHEPTANE	117.7	0.0024	0.0119	0.0107	8.0	P
58	3-METHYLHEPTANE	117.0	0.0022	0.0071	0.0068	8.0	P
59	2,2,5-TRIMETHYLHEXANE	124.0	0.0073	0.0081	0.0079	9.0	P
60	N-OCTANE	125.0	0.0019	0.0076	0.0077	8.0	P
61	2,3,5-TRIMETHYLHEXANE	131.3	0.0012	0.0018	0.0030	9.0	P
62	2,4-DIMETHYLHEPTANE	133.5	0.0007	0.0014	0.0028	9.0	P
63	2,5-DIMETHYLHEPTANE	136.0	0.0009	0.0024	0.0035	9.0	P
65	ETHYLBENZENE	136.2	0.0091	0.0116	0.0101	8.0	A
68	M-XYLENE	139.1	0.0249	0.0454	0.0298	8.0	A
69	4-METHYLOCTANE	141.0	0.0000	0.0000	0.0000	9.0	P
70	3-METHYLOCTANE	143.0	0.0009	0.0038	0.0052	9.0	P
71	O-XYLENE	144.0	0.0154	0.0244	0.0183	9.0	A
176	2-METHYLOCTANE	142.8	0.0005	0.0014	0.0035	9.0	P
177	TRANS-2-NONENE	0.0	0.0017	0.0027	0.0037	9.0	O
72	NONANE	150.8	0.0030	0.0016	0.0031	9.0	P
73	N-PROPYLBENZENE	159.0	0.0086	0.0069	0.0076	9.0	A
84	M-ETHYLTOLUENE	161.0	0.0321	0.0271	0.0206	10.0	A
154	1,3,5-TRIMETHYLBENZENE	164.7	0.0137	0.0110	0.0094	9.0	A
86	O-ETHYLTOLUENE	162.0	0.0147	0.0150	0.0138	10.0	A
180	CIS-PROPYLBENZENE	159.2	0.0007	0.0027	0.0035	9.0	A
78	1,2,4-TRIMETHYLBENZENE	169.3	0.0439	0.0373	0.0308	9.0	A
79	SEC-BUTYLBENZENE	173.0	0.0016	0.0025	0.0017	10.0	A
80	N-DECANE	174.0	0.0000	0.0000	0.0000	10.0	P
99	1,2,3-TRIMETHYLBENZENE	176.1	0.0121	0.0119	0.0115	9.0	A
181	INDANE	176.5	0.0063	0.0062	0.0067	9.0	A
182	4-PHENYL-1-BUTENE	177.0	0.0046	0.0042	0.0062	10.0	A
183	1-METHYL-3N-PROPYLBENZENE	0.0	0.0127	0.0114	0.0102	10.0	A
118	1,3-DIETHYLBENZENE	181.0	0.0075	0.0067	0.0061	10.0	A
100	BUTYLBENZENE	183.0	0.0095	0.0081	0.0076	10.0	A
120	1,2-DIETHYLBENZENE	183.4	0.0065	0.0056	0.0031	10.0	A
208	1-METHYLNAPHTHALENE	212.0	0.0132	0.0183	0.0148	11.0	A
153	NAPHTHALENE	211.0	0.0155	0.0152	0.0151	10.0	A
186	1-UNDECENE	192.7	0.0065	0.0051	0.0072	11.0	O
92	UNDECANE	195.0	0.0066	0.0074	0.0072	11.0	P
87	TERT-BUTYLBENZENE	169.0	0.0098	0.0076	0.0099	10.0	A
81	UNKNOWNS	-122.5	0.0975	0.0784	0.1222	1.0	U

Table 10. Comparison of Original MSERB Species Identifications (Left) with UNC Modified Species Identifications (Center) with Feb. 1985 MSERB Species Identifications (Right).

ID#	ORIGINAL MSERB	ID#	UNC	ID#	REVISED MSERB
1	METHANE	1		1	
2	ETHYLENE	2		2	
3	ETHANE	3		3	
4	ACETYLENE	4		4	
5	PROPYLENE	5		5	
5	PROPANE	6		5	
6	PROPADIENE	7		6	
7	METHYL ACETYLENE	8		7	
8	ISOBUTANE	9		8	
9	1-BUTENE	10		9	
9	ISOBUTYLENE		Not Reported	9	
10	N-BUTANE	12		10	
10	1,3-BUTADIENE	13		10	
11	TRANS-2-BUTENE	14		11	TRANS-2-BUTENE
					2,2-DIMETHYLPROPANE
12	CIS-2-BUTENE	15		12	CIS-2-BUTENE
					1-BUTYNE
13	3-METHYL-1-BUTENE	16		13	
14	ISOPENTANE	17		14	
15	1-PENTENE	18		15	1-PENTENE
					2-BUTYNE
16	N-PENTANE	19		16	
16	2-METHYL-1-BUTENE	20			Not Reported
17	2-METHYL-1,3-BUTADIENE	175		17	
18	TRANS-2-PENTENE	21		18	
19	CIS-2-PENTENE	22		19	
20	PENTYNE	189			Not Reported
21	2-METHYL-2-BUTENE	83		20	
					2,2-DIMETHYLBUTANE
22	CYCLOPENTENE	24		22	
23	CYCLOPENTANE	25		23	CYCLOPENTANE
					3&4-METHYL-1-PENTENE
24	2,3-DIMETHYLBUTANE	27		24	
25	2-METHYLPENTANE	28		25	
25	2,3-DIMETHYL-1-BUTENE		Not Reported	25	
26	3-METHYLPENTANE	30		26	
27	1-HEXENE	31		27	
27	2-ETHYL-1-BUTENE		Not Reported	27	
28	N-HEXANE	33		28	
28	CIS-3-HEXENE		Not Reported	28	
				29	C6 OLEFIN
29	2-METHYL-2-PENTENE	35		30	
30	CIS-2-HEXENE	96		31	CIS&TRANS-2-HEXENE
31	HEXYNE	188			Not Reported
32	METHYLCYCLOPENTANE	36		32	
32	3-METHYLTRANS-2-PENTENE		Not Reported	32	
33	2,4-DIMETHYLPENTANE	38		33	
34	METHYLCYCLOPENTENE	39		34	
35	BENZENE	40		35	
35	CYCLOHEXANE		Not Reported		Not Reported
36	CYCLOHEXENE	41		36	
36	2,3-DIMETHYLPENTANE		Not Reported	36	
36	2-METHYLHEXANE		Not Reported	36	
37	3-METHYLHEXANE	44		37	

Table 10 cont. Comparison of Original MSERB Species Identifications (Left) with UNC Modified Species Identifications (Center) with Feb. 1985 MSERB Species Identifications (Right).

38	2,2,4-TRIMETHYLPENTANE	82	
39	N-HEPTANE	47	
40	2,4,4-TRIMETHYL-1-PENTENE	48	
40	3-METHYLHEXANE		Not Reported
41	METHYLCYCLOHEXANE	49	
42	1-CIS-4-DIMETHYLCYCLOHEXANE	50	
43	2,4-DIMETHYLHEXANE	51	
43	2,5-DIMETHYLHEXANE		Not Reported
44	2,3,4-TRIMETHYLPENTANE	53	
45	2,3,3-TRIMETHYLPENTANE	54	
46	TOLUENE	55	
46	2,3-DIMETHYLHEXANE		Not Reported
47	2-METHYLHEPTANE	57	
48	4-METHYLHEPTANE	157	
49	3-METHYLHEPTANE	58	
50	2,2,5-TRIMETHYLHEXANE	59	
51	N-OCTANE	60	
52	2,3,5-TRIMETHYLHEXANE	61	
53	2,4-DIMETHYLHEPTANE	62	
54	2,5-DIMETHYLHEPTANE	63	
54	3,5-DIMETHYLHEPTANE		Not Reported
55	ETHYLBENZENE	65	
55	2,3-DIMETHYLHEPTANE		Not Reported
56	M-XYLENE	68	
56	P-XYLENE		Not Reported
57	4-METHYLOCTANE	69	
58	3-METHYLOCTANE	70	
59	O-XYLENE	71	
59	UNK C9 PARAFFIN		Not Reported
60	2-METHYLOCTANE	176	
61	TRANS-2-NONENE	177	
62	NONANE	72	
63	N-PROPYLBENZENE	73	
64	1,3,5-TRIMETHYLBENZENE	84	M-ETHYLTOLUENE
65	2,3-DIMETHYLOCTANE	154	1,3,5-TRIMETHYLBENZENE
66	METHYL CYCLOOCTANE	86	O-ETHYLTOLUENE
67	CIS-PROPYLBENZENE	180	
68	1,2,4-TRIMETHYLBENZENE	78	
69	SEC-BUTYLBENZENE	79	
70	N-DECANE	80	
71	1,2,3-TRIMETHYLBENZENE	99	
72	INDANE	181	
73	4-PHENYL-1-BUTENE	182	
74	1-METHYL-3N-PROPYLBENZENE	183	
75	1,3-DIETHYLBENZENE	118	
76	N-BUTYLBENZENE	100	
77	1,2-DIETHYLBENZENE	120	
78	2-METHYLDECANE	208	1-METHYLNAPHTHALENE
79	CYCLOPENTYLCYCLOPENTANE	153	NAPHTHALENE
80	1-UNDECENE	186	
81	UNDECANE	92	
82	TRANS-1-PHENYLBUTENE-1	87	TERT-BUTYLBENZENE
83	UNKNOWNS	81	

38	
39	
	Not Reported
	Not Reported
40	
41	DIMETHYL-HEXENE
42	2,2-DIMETHYLHEXANE
43	
43	
44	
45	
46	
46	
47	2-METHYLHEPTANE
47	1-METHYLCYCLOHEXENE
48	
49	
50	
51	
52	
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54	
54	
55	
55	
56	
56	
57	2-METHYLOCTANE
58	2,4,5-TRIMETHYLHEPTANE
59	
59	
60	2,4-DIMETHYLOCTANE
	Not Reported
61	
62	UNKNOWN(C10 PARAFFIN?)
63	
64	
65	3,4-DIMETHYLOCTANE
66	1-METHYL/3-ETHYLBENZENE
67	1-METHYL/2-ETHYLBENZENE
68	
69	
70	
71	
72	
73	ISOBUTYLBENZENE
74	
75	
76	1-METHYL/3-ISOPROPYLBENZENE
77	
78	
79	C10 AROMATIC
80	C10 AROMATIC
81	
82	C10 AROMATIC
83	

D

Calibration of NMHC

The purpose of this appendix is to describe how the Beckman 6800 Total Hydrocarbon/ Methane gas chromatographic analyzer was calibrated for this study. Because the discussion becomes somewhat complicated without reference to an example, the example instrument output from Appendix B has been included here as Figure 1.

As shown in Figure 1 this instrument produced three peaks on its output stripchart recorder. Four cycles are shown in Figure 1, two for one side of the chamber and two for the other side of the chamber. The peak marked (1) in Figure 1 is designated the THC peak. It was created by sending the entire air sample with all of the HC together, to the flame ionization detector (FID). The peak marked (2) is called the methane peak. It was created by chromatographically separating the CH_4 in the sample from the other HCs in the sample and sending only the CH_4 to the FID detector (the transient just before peak (2) was caused by a valve switch between the THC mode and the CH_4 mode). The peak marked (3) in Figure 1 is the CO peak that was also chromatographically separated and then converted to CH_4 before being sent to the FID. This appendix will not discuss the CO peak nor its calibration.

The FID is supposed to act as a "carbon counter" system, producing a certain amount of signal for each carbon found in the sample. The *ideal* FID detector's output is independent of HC species identity, that is, the signal from 1 ppmV of methane would be exactly the same as the signal from 0.5 ppmC of ethane (or ethylene). When used in a chromatographic-like mode, most FID detectors are

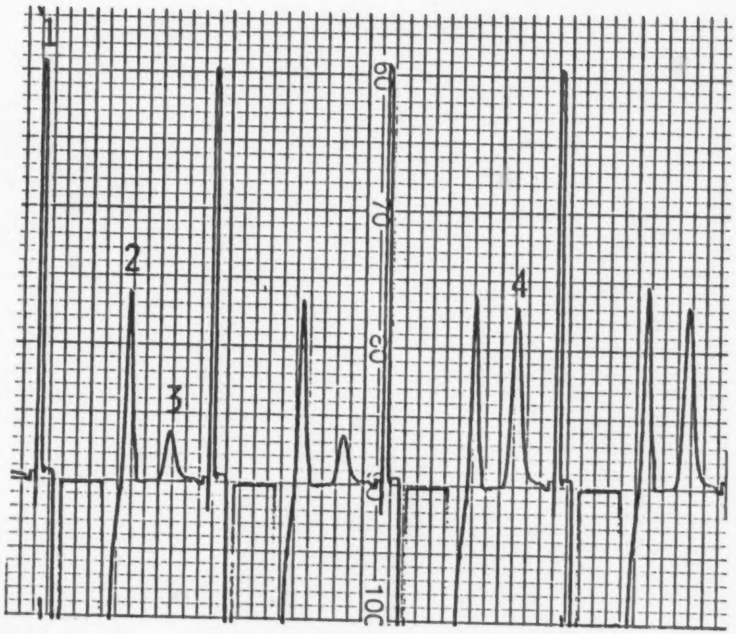

Figure 1. Example Chromatograms from Beckman 6800 Gas Chromatograph. Peaks: (1) Total Hydrocarbons — 4.0 ppmC, Attenuation × 2; (2) Methane — 2.5 ppmC, Attenuation × 1; (3) CO — 9.9 ppmC, Attenuation × 2; (4) CO — 37.2 ppmC, Attenuation × 2.

nearly ideal. When used in a THC-like mode, however, a problem occurs. Methane's response on the THC mode is often lower than the response of higher HCs such as propane and ethylene. Therefore if CH_4 and another non-methane HC were both present in equal concentrations, CH_4 would not contribute as much to the THC peak height as the other species would contribute.

The common method of converting the THC-signals and the CH_4-signals to concentrations is to multiply the peak height (units of inches) by a calibration factor (with units of ppmC/inch). The calibration factors are normally created by having the Beckman 6800 sample a standard known source of CH_4 and NMHC in air. The calibration factors are then calculated by dividing the concentration by the peak height produced. Since CH_4 is separated from NMHC the calculation of the calibration factor is straight forward:

$$\mathrm{CH_4 as\ CH_4(ppmC/inch)} = \frac{\mathrm{source\ CH_4(ppmC)}}{\Delta\ \mathrm{peak\ (2)\ height\ (inches)}} \tag{1}$$

The inverse of this calibration factor is the response factor which will be called z below.

If a single calibration source containing both CH_4 and NMHC was used, however, the problem of the two-tiered response on the THC analysis prevents such a straight forward calculation for the NMHC. That is, the THC signal can be expressed as

$$\Delta\ \mathrm{peak\ (1)\ height\ (inches)} = \frac{x\ \mathrm{inches}}{\mathrm{ppmC\ CH_4}} \times \Delta[\mathrm{CH_4}] + \frac{y\ \mathrm{inches}}{\mathrm{ppmC\ NMHC}} \times \Delta[\mathrm{NMHC}] \tag{2}$$

where x and y are different values.

If $[CH_4]$ is constant, as in typical chamber injections, then only the $1/y$ calibration factor would be needed to calculate how much [NMHC] was injected from Δ(peak(1) height).

The only way, however, to calculate how much [NMHC] was injected when the injection source also contains CH_4 is to know both $1/y$ and $1/x$ values. This requires that two calibration sources be used: one containing CH_4 as the only HC and one containing NMHC which may or may not contain CH_4 as well. Thus three calibrations must be performed:

- the CH_4 response must be determined as CH_4 on the methane output (*i.e.* peak 2)—the z value;

- the CH_4 response must be determined as THC on the total hydrocarbon output (*i.e.* peak 1)—the x value;
- the NMHC response must be determined as THC on the total hydrocarbon output (*i.e.* peak 1)—the y value.

Using $1/z$, one can determine how much CH_4 was injected and then using x, one can calculate a "correction" to the THC peak height; the "corrected" peak height can then be converted to [NMHC] using $1/y$.

Table 1 is an example of these calculations for the July 2, 1983 experiment in which automobile exhaust was injected into the BLUE chamber. Across the top of the table are listed the peak heights of the methane peak (*i.e.* peak 2) and the total hydrocarbon peak (*i.e.* peak 1) before injection (called "background") and after the exhaust injection (called "final"). Peak 2 changed by 0.120 inches and peak 1 changed by 1.09 inches.

Next the table lists the calibration factors: NMHC as THC (which is $1/y$); CH_4 as THC (which is $1/x$); and CH_4 as CH_4 (which is $1/z$). These were determined by use of calibration tanks, and the calculations based upon these values are shown further in the table as "Cal Factors from Tank Sources."

The first calculation was to compute how much CH_4 was injected

$$0.120 \text{ inches} \times 2.1498 \text{ ppmC/inch} = 0.258 \text{ ppmC}$$

Next, this concentration of CH_4 was converted to a Δpeak height for peak 1 using the CH_4 as THC calibration factor

$$\frac{0.258 \text{ ppmCCH}_4}{1.3191 \text{ ppmC/inch}} = 0.1956 \text{ inches}$$

Then the original Δpeak-height of 1.09 inches for the THC was reduced by the signal caused by CH_4

$$1.090 \text{ inches} - 0.1956 \text{ inches} = 0.894 \text{ inches}$$

which was the effective signal caused by the NMHC injected. This Δpeak-height was converted to a concentration using the NMHC as THC calibration factor

$$0.894 \text{ inches} \times 1.8506 \text{ ppmC/inch} = 1.655 \text{ ppmC}$$

which was the injected NMHC.

This describes the technique used in the 1983 data processing.

In 1982, the response of CH_4 on the THC signal was not determined routinely. Therefore the response factor, x, must be estimated for this year's Beckman 6800 NMHC data. Examples of these calculations are also included in Table 1.

The first source depends upon the natural background levels of CH_4 at the chamber site. This value has been measured for more than 10 years using a variety of NMHC analyzers and gas chromatographs. The average value is 1.60 ppmC CH_4. Most measurement techniques for CH_4 have a precision (repeatability) of ±0.05 ppmC for this measurement. In addition, there is some NMHC background at the chamber; we have assumed for purposes of calculation that this value is 0.2 ppmC. As will be seen, this value has little effect on the overall calculation.

If the background CH_4 is assumed to be the cause of the insturment's "background" response for CH_4, a calibration factor for CH_4 as CH_4 can be derived. For example, Table 1 lists (on the right hand side) the assumed background CH_4 and NMHC. Using these values, the calibration factor for CH_4 as CH_4, $1/z$, can be computed as

$$\frac{1.60\text{ ppmC}}{1.08\text{ inches}} = 1.4815\text{ ppmC/inch}$$

and this value is listed under "`Cal Factors`" as "`CH4 Air`".

This calibration factor can be used to calculate how much CH_4 was injected from the exhaust as

$$1.4815 \times 0.120 = 0.178\text{ ppmC}$$

.

Next, the assumed background of NMHC of 0.2 ppmC and the tank derived calibration factor for NMHC as THC were used to arrive at a "correction" to the background THC peak height. This was done as

$$\frac{0.20\text{ ppmC}}{1.8506\text{ ppmC/inch}} = 0.108\text{ inches}$$

and

$$\frac{1.60\text{ ppmC}}{(1.65\text{ inches} - 0.108\text{ inches})} = 1.038\text{ ppmC/inch}$$

The response of the THC signal to the injected CH_4 was calculated as

$$\frac{0.178 \text{ ppmC } CH_4}{1.038 \text{ ppmC/inch}} = 0.171 \text{ inches}$$

At this point the calculations were the same as in the first case and the NMHC injected was calculated to be 1.700 ppmC or 0.045 ppmC higher (2.7% more than when full calibration was used).

The last form of the calculation was based on measurement of CH_4 using the gas chromatograph Carle II which is able to separate CH_4. Carle II is connected to the Sigma Integrator and the integrator has been programmed with a calibration factor based on the Carle II average performance and the assumption that the chamber background CH_4 concentration is 1.60 ppmC. On this day, the Carle II and integrator reported the chamber background as 1.545 ppmC which is within 3.5% of the assumed background, consistent with the discussion above on precision of this measurement. It reported 1.664 ppmC CH_4 after the injection giving a value of 0.119 ppmC CH_4 injected.

At this point, the calculation was the same as in the second case and the NMHC injected was calculated to be 1.805 ppmC or 0.150 ppmC higher (9% more NMHC than when a full calibration was used).

Thus we believe the calibrations in 1982 were within 10% of the values that would have been reported if full calibration had been used.

The NMHC as THC calibration factors are the critical values in each of these procedures and these values were within ±10% of the mean calibration factor for the whole 1983 data season.

We believe to total uncertainty in the reported NMHC values to be ±12%.

TABLE 1. NMHC CALCULATIONS - CORRECTION FOR METHANE AS THC

Run Date: July 2, 1983 Side: BLUE

Peak Height (in)				Cal Factors (ppmC/in)					Background Assumptions (ppmC)		Carle II CH4 Measurements (ppmC)	
CH4		THC		Tank			Air CH4					
background	final	background	final	NMHC as THC	CH4 as THC	CH4 as CH4	CH4 as THC	CH4 as CH4	NMHC	CH4	Before	After
1.08	1.2	1.65	2.74	1.8506	1.3191	2.1498	1.038	1.481	0.2	1.6	1.545	1.664

NMHC Calculations with all Cal Factors from Tank Sources

CH4 Inj (ppmC) (tank cal)	CH4 Inj (in) on THC	NMHC Inj (in)	NMHC Inj (ppmC)
0.258	0.196	0.894	1.655

NMHC Calculations with CH4 Cal Factors from Air CH4

CH4 Inj (ppmC) (air cal)	CH4 Inj (in) on THC	NMHC Inj (in)	NMHC Inj (ppmC)
0.178	0.171	0.919	1.700

NMHC Calculations with CH4 Cal Factors from Air CH4 and Carle2 Measured Methane Injected

CH4 Inj (ppmC) (Carle II)	CH4 Inj (in) on THC	NMHC Inj (in)	NMHC Inj (ppmC)
0.119	0.115	0.975	1.805